CO-ORDINATION CHEMISTRY OF TRANSITION METALS INVOLVING NITROGEN, SULFUR AND OXYGEN DONOR LIGANDS

ABSTRACT

THESIS

SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

BY

DEVENDRA KUMAR

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

1992

ABSTRACT

Reaction of 4-cyano-5-aminopyrazole, $H4CN5NH_2pz$ in EtOH with anhydrous transition metal chlorides and group IIB metal chlorides, MCl_2 [M=Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)] in THF afforded the isolation of the complexes of the type, ML_4Cl_2 [L=$H4CN5NH_2pz$]. The complexes are soluble in most non-polar solvents. The complexes have been characterized on the basis of elemental analysis, molecular weights, magnetic susceptibility measurements, infrared and electronic spectral studies. The results of elemental analysis of these compounds corresponds to their composition [ML_4Cl_2]. The i.r. spectra of these compounds recorded on KBr discs exhibit well resolved bands which have been assigned comparing with the bands obtained for free ligand. A positive shift in N-H mode attributable to differences in the internal or external hydrogen bonding indicate the coordination of L via pyridyl nitrogen N(2) which has been further substantiated by a negative shift (5-15 cm^{-1}) in νC=N. However, the bands corresponding to CN and NH_2 groups appar almost in the same frequency regions as observed in the free ligand, ruling out coordination of CN and NH_2 to the metal ions.

The observed low electrical conductivity values for 1mM solution in DMSO suggest their non-ionic nature. However, the

experimentally determined molecular weights confirm their monomeric nature. The observed values of magnetic moments are reasonably consistent with an octahedral geometry of these compounds. The positions of the bands observed both in the reflectance and electronic spectra are comparable and provide further confirmation of the proposed octahedral geometry.

Reactions of ammonical solution of metal (I) chlorides with 4-cyano-5-aminopyrazole, H4CN5NH_2pz or 3,4-dicyano-5-aminopyrazole, H3,4 $(CN)_2$5NH_2pz afforded the formation of colorless, sticky and insoluble polymeric complexes of the types [M(4CN5NH_2pz]$_n$ or [M3,4 $(CN)_2$5NH_2pz]$_n$ (M=Cu or Ag). However, pyrazolide-bridged dimeric species, [M(PPh_3)$_2$ (4CN5NH_2pz)]$_2$ or [M(PPh_3)$_2$ (3,4 $(CN)_2$5NH_2pz)]$_2$ soluble in most non-polar solvents were obtained from the precursors, [M(PPh_3)$_3$X] [M=Co, Cu, Ag] under similar reaction conditions. The analytical data of these compounds either obtained from metal(I) chlorides of their triphenylphosphine derivatives suggest that the complexes are formed in 1:1 stoichiometry. The bands observed in the i.r. spectra of these compounds have been assigned comparing with that observed for free ligands. The complete absence of N-H stretching mode and a slight negative shift (10-30cm^{-1}) in the νC=N vibration of the pyrazole ring suggest the formation of pyrazolide ion in basic medium, [4CN5NH_2pz]$^-$ or [3,4 $(CN)_2$5NH_2pz]$^-$ which coordinate both the nitrogens, i.e. pyridyl N(2) as well as pyrolic N(1).

The presence of coordinated PPh_3 groups which restrict the polymerization of these compounds has been confirmed by the characteristic bands of PPh_3 as well as M-P. All the complexes are diamagnetic as expected.

Reaction of 3-mercapto-1, 2-propanediol and its 1-methoxy and 1-ethoxy derivatives, $HSCH_2CH(OH)\ CH_2OR'$ ($R'=H$, CH_3, C_2H_5) [RSH, $R=CH_2CH(OH)CH_2OR'$] with $[M(PPh_3)_3\ X]$ [M=Co(I), Cu(I); X=Cl or Ag(I); $X=NO_3$] in THF yield bridged dimeric species. $[M(PPh_3)_2\ RS]_2$ [$R=CH_2CH(OH)CH_2OR'$; M=Co(I) (1), Cu(I) (2), Ag(I) (3); (1a), (2a), (3a) and (1b), (2b), (3b) for $R'=H$, CH_3 and C_2H_5 respectively]. The complexes corresponding to Co(I) and Cu(I) are also prepared by reaction with $[M(PPh_3)_2\ Cl_2]$ under similar reaction conditions. $[M(PPh_3)_2\ RS]_2$ [M=Co(1'), Cu(2'); (1a'), (2a') and (1b'), (2b') for R=H, CH_3, C_2H_5 respectively where the metal ions have been reduced to their corresponding monovalent states.

The results of elemental analysis suggest that the complexes either derived from $[M(PPh_3)_3\ X]$ or $[M(PPh_3)_2Cl_2]$ are formed in 1:1 stoichiometry with the composition $[M(PPh_3)_2RS]_2$. However, the reaction of RSH with $[M(PPh_3)_3\ X]$ results in the libration of one equivalent of free PPh_3. The experimental molecular weights confirm the dimeric nature, whilst the low electrical condunctivity values reveal the covalent nature of these compounds.

The IR spectra of all the compounds when compared with the free ligands, RSH show the complete absence of the νS-H alongwith the two new medium intensity bands in 340-390 cm^{-1} region corresponding to νM-S suggest the coordination via sulphur atom of mercaptide group. The non-involvement of primary oxygen of the ligand in coordination has been inferred by comparing the position of ν(C-O) (1060-1070 cm^{-1}) with that observed for bridged OCH_3 or OC_2H_5 groups in metal alkoxides. The bands characteristic of PPh_3 and ν(M-P) appear in their expected positions. The magnetic moment values recorded for the compounds derived from $[Co(PPh_3)_3Cl]$ or $[Co(PPh_3)_2Cl_2]$ are comparable to that reported for Co(I) complexes having tetrahedral geometry which is further substantiated by an intense band in the reflectance spectra of these compounds centerd in the 14,690--14,800 cm^{-1} region corresponding to $^3T_{1g}(P) \longleftarrow {}^3T_{1g}(F)$ transition. However, the measurements on the magnetic properties of complexes obtained from $[Cu(PPh_3)_3Cl]$, $[Ag(PPh_3)_3NO_3]$ or $[Cu(PPh_3)_2Cl_2]$ indicate their diamagnetic nature.

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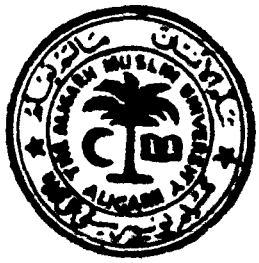

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Dedicated
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My Parents

DIVISION OF INORGANIC CHEMISTRY
DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202002 (INDIA)

MOHAMMAD SHAKIR
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Phone office 25515
Dated..... .....

CERTIFICATE

Certified that the work embodied in this thesis entitled '**CO-ORDINATION CHEMISTRY OF TRANSITION METALS INVOLVING NITROGEN, SULFUR AND OXYGEN DONOR LIGANDS**' is the original research work carried out by Mr. Devendra Kumar, under my supervision. This work is suitable for the submission of the award of **Ph.D.** degree of Aligarh Muslim University, Aliagrh.

24/IX/92

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Date : 24/X/92

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He possess that talent which proves to me a substitute for all treasure and which in my mind is stimulus for the complete analysis of all his useful or desirable suggestion to be acquainted with me throughout my work.

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(Devendra Kumar)

LIST OF PUBLICATION

1. 4-Cyano-5-Aminopyrazole as Ligand; Synthesis and charaterization of its complexes with Cr (II), Mn (II), Zn (II), Cd (II) and Hg (II).
   Indian J.Chem., 29A, 919 (1990).

2. Coordinating Behaviour of 4-Cyano-5-aminopyrazole Lignad; Synthesis and physico-chemical studies of some transition metal complexes ML_4Cl_2 [M = Fe, Co, Ni, Cu, L = $H4CN5NH_2pz$].
   Synth. React. Inorg. Met.-Org. Chem., 20(9), 1241 (1990).

3. Complexes of 1,2-Dihapto 4-Cyano-5-Aminopyrazolide Ion with Metal (I) Chlorides, MCl and Their Triphenylphophine Derivatives $[M(PPh_3)_3X]$ [M = Cu and Ag for X = Cl and NO_3 respectively].
   Transition Met. Chem., 16, 631 (1991).

4. Complexes of 3-mercapto-1,2-propanediol and its 1-methoxy and 1-ethoxy derivatives, $HSCH_2CH(OH)CH_2OR'$ (R'= H, CH_3, C_2H_5) with triphenylphophine derivatives of Co (I), Co (II), Cu (I), Cu (II) and Ag (I) ions.
   Polyhedron (In press), 1992.

5. Transition metal complexes of Schiff base macrocycles containing the furanyl moiety.
   Transition Met. Chem., (Accepted), 1992.

CONTENTS

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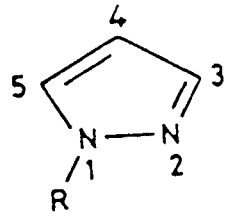
CHAPTER - I
INTRODUCTION

INTRODUCTION

The importance and scope of studies on coordination chemistry of pyrazole could be assessed from the enormous interest shown by many workers, and the work appearing in literature during recent years on the coordination chemistry of pyrazole leading to development of many interesting areas. A brief survey of work on pyrazole will be helpful in bringing out the importance and scope of a part of this project.

The pyrazoles, Rpz(R=H, alkyl or aryl groups) (I) are thermallly and hydrolytically very stable moieties, which have been found to coordinate to metals and metalloids through pyridyl nitrogen N(2) if the reactions are performed in neutral medium. A survey of literature has revealed a variety of complexes of these 2-monohaptopyrazoles, Rpz^{1-5} (Fig.1).



(R = H, Me, Ph)

Fig. 1

The simplest and most thoroughly studied types of

pyrazole complexes are $[M(Hpz)_nX_m]$ where M = transition metals, Hpz = 2-monohaptopyrazoles, X = counter ions, m = valence state of the transition metals, usually divalent. These complexes are prepared readily by the reaction of metal salts with pyrazoles (Hpz) in neutral or slightly acidic medium as shown below :

$$MX_2 + nHpz \longrightarrow [M(Hpz)_nX_2] \qquad (1)$$

The complexes thus derived have been reported [1-5] to coordinate via pyridyl nitrogen N(2) of the five membered ring. This has been further confirmed by X-ray crystallography[6-10]. However, the number of pyrazoles coordinated to the metal ions depends on the following factors.

1. Coordinating ability of counter ion

A variety of the complexes of the type $[M(Hpz)_n]X_m$ (n=6 and m=2) have been found to show maximum coordination of the pyrazoles if X is a non-coordinating anions, viz NO_3, BF_4 or ClO_4 and M=Mn(II), Co(II), Ni(II), Zn(II) or Cd(II). However, the complexes of the type $[M(Hpz)_n]X_m$ (n=4 and m=2) have been reported[1] for X = halide ion when M = Ni, Cu and Fe. The structure of these complexes have been further confirmed by X-ray crystallography[6-10]. In the complexes, however, the halogens are coordinated to Ni placing it again in a octahedral environment. The pyrazole rings are oriented

vertically with respect to plane defined by the Ni atom and the four coordinated nitrogens and there exists a hydrogen bond between the N(1) and the halogen in both compounds.

2. **Nature of the metal ions**

It has been reported that Cu(II) never give the complex of the type $[Cu(Hpz)_6]X_2$ under any conditions, rather it produce only tetracoordinate complexes of the type $[Cu(Hpz)_4]X_2$ regardless of the nature of counter anion (X=Cl, Br, BF_4, ClO_4 SO_4, NO_3)[1,11,12]. The presence of substituents viz. Cl, Br, NO_2 or of 1-Me at 4-position of pyrazole ring did not alter the maximum CuL^{2+} stoichiometry[13].

3. **Substitution on the pyrazole ring**

A substituent in the 3-position introduces steric hindrance and makes it difficult to have six 3-substituted pyrazoles coordinated via the N(2) to a metal. This difficulty can be circumvented by coordination through a tautomeric 5-substituted structure, where steric hindrance is minimized. In fact, the highest apparent coordination number for a variety of transition metal ions, (Mn, Fe, Co, Cd) has been reported[2] in the structure of the type $[M(H3\text{-}Mepz)_7](ClO_4)_2$ although the seventh pyrazole is regarded as being in the second coordination sphere. By contrast, $H3,5\text{-}Me_2pz$ which has both positions adjacent to the nitrogens substituted with methyl groups forms only complexes of the type $[M(H3,5\text{-}Me_2Pz)_4]X_2$[14]. However, 4- methylpyrazole has the

methyl group far from coordination site and, consequently, it behave like pyrazole itself[2].

Coordination compounds of a few substituted pyrazoles viz. methylpyrazole, dimethylpyrazole, trimethylpyrazole, nitro-pyrazole, chloropyrazole and bromopyrazole with first row transition metals have been studied[2,15-19] where the number of substituted pyrazole molecules has been generally found to be four except for the complexes derived from metal halide[2,15] having only two of the ligand molecuIs coordinated to metal ions. The bis-complexes of nickel halides with pyrazole and dimethylpyrazole have trans $[Ni(Pz)_2X_4]$ units in polymeric halogen bridged structures[15]. However, 3,5 - Dimethylpyrazole [H3,5-Me_2pz] on reacting with an excess of cupric chloride yeilds the complex $Cu(Me_2pz)Cl_2$[17] also having a halogen bridged structure (II).

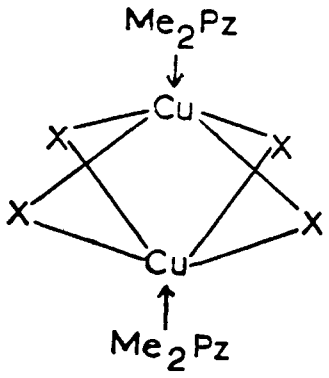


Fig. 2

In view of forgoing discussion it is apparent that the

coordination number decreases with the increase in bulk of the ligand used.

The i.r. spectra of the complexes of pyrazoles have been reported to be scarcely different from that of the free ligand except the position of the N-H str. band which has been reported to undergo a positive shift in all the complexes[20]. Moreover, Reedijk et al[21] have observed a splitting of N-H mode in the Cu(II) complexes of pyrazole and substituted pyrazoles and has been explained in terms of unequal hydrogen bonding in one complex unit. However, the position and intensity of N-H band has been found to be strongly dependent upon the nature of the anion in combination with the metal ion as evident from the following decreasing order as the N-H stretching mode in complexes derived from nickel(II) salts with 3,5 - dimethylpyrazole salts that the N-H stretching frequency decreased with the change in the anion in the following manner[20].

$$ClO_4 > BF_4 > I > NO_3 > Br > Cl$$

The occurence of this particular sequence of anions with respect to N-H stretching has been explained in terms of the increasing hydrogen bonding of the ligand with these anions resulting in the lowering in N-H frequency.

It is noteworthy that in all the complexes the

coordination of pyrazoles or substituted pyrazoles to the metal ions has always been shown[17-19] to be only through pyridyl nitrogen, N(2) and in no case through the pyrrolic nitrogen N(1). The pyrazole nucleus as such has always been found to behave as a monodentate ligand even in the complexes where only two molecules of ligands are coordinated to the metal ions.

A detailed study of electronic spectra of $M(H5Mepz)_2X_2$ for M=Mn, Fe, Co, Ni and Cu, and X = NO_3, Cl, Br, I, ClO_4 and BF_4 showed considerable distortion from octahedral symmetry. This was attributed in terms of hydrogen bonding between the ligand and the anion. IR and Raman spectra of these complexes show the N-H vibration to be strongly dependent on hydrogen bonding which was found to be greatest with chloride anion[6], followed by Br, I, NO_3 and BF_4, while no hydrogen bonding was observed for ClO_4. However, the complexes of the type CoL_4X_2 (X = Cl, Br, or SCN) have been prepared[18] with 3,5-dimethylpyrazole, while a tetrahedral complexes of the type $ML_2(SCN)_2$ have been reported[22] for Zn and Cd.

Although it has generally been assumed that Hpz and Rpz coordinate exclusively through the substituted N(2) (the 'pyridyl'N), in line with all the structures that have been established by X-ray crystallography. However, in some instance data have been interpreted to imply coordination through the substitued N(1) ('pyrrolic'N). Thus, paramagnetic

shift in 1-vinyl-2-methyl-and 1-ethyl-2-methylpyrazolium iodides in presence of $CoCl_2$(1-ethyl-imidazole)$_4$ were interpreted as implying coordination of the pyrrolic nitrogen[23] as the paramagnetic shifts were observed[24] in coordination of Hpz in the following complexes.

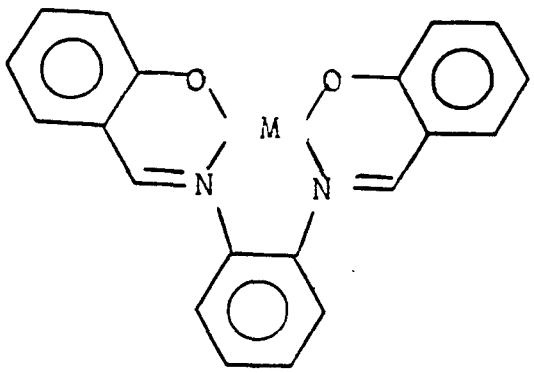


Fig. 3

Complexes of H3, 5-Me_2Pz and R3Me5NH_2Pz (R=H, Me, Ph) with a variety of trialkyl borane have been prepared and characterized. All ligands bond through N(2), except for Ph3Me5NH_2Pz, which bonds via NH_2[25].

Apart from complexes of the first row transition metals, pyrazole complexes of ruthenium in several oxidation states have also been investigated. The blue solution of Ru(II) when treated with payrazole or 3,5-dimethylpyrazole, produced species such as RuL_3Cl_3, $RuL_3Cl_2(H_2O)$ etc. characterized by

analysis and conductivity data[26]. The complexes of the type L_2AgNo_3 and $L_2(HgCl_2)_3$, where L = 3(5)- methylpyrazole, have also been reported[27].

In addition to complexing with simple transition metal ions pyrazoles have been reported to coordinate with diverse organometallic species. Thus, the reaction of pyrazole with $C_5H_5CoI_2CO$ results in the displacement of CO and the formation $C_5H_5CoI_2(Hpz)$ as an air-stable green solid species[28]. Simple coordination by pyrazole to relieve coordinative unsaturation has been reported[29,30] for $Et_2B(Pz)_2$ $Mn(CO)_2$-π-allyl and for compounds such as $H_2B(Pz)_2Mn(CO)_3$[31]. In each of these instances the addition of pyrazole gives rise to a inert gas configuration. The reaction of $Fe(CO)_5$ with 3,5-dimethyl-pyrazole is reported[32] to give air sensitive $(H3,5\text{-}Me_2pz)_2$ FeCO as a pink solid. A π-bonded sandwich structure has been tentatively proposed for this compound; this however, seems unlikely. The above results constrast with the reaction of iron pentacarbonyl with pyrazole itself where $[Fe(Pz)_2]_n$ has been obtained[33].

The reaction of 3,5-dimethylpyrazole with chromium-hexacarbonyl yields only the $LCr(CO)_5$ at any reactant ratios, while with tungsten hexacarbonyl either $LW(CO)_5$ or $L_2W(CO)$ may be obtained[34]. Another complex containing both pyrazole and carbonyl ligand is $RuCl_2(CO)_2(HPz)_2$[34,35,36].

The ability to lose the 1 proton and to function as a

uninegative, exobidentate 1,2-dihapto ligand in basic medium having C_{2v} symmetry is a characteristic feature of pyrazole. The geometry of pyrazolide ion permits it to act as a bridge between two identical or dissimilar metals or metalloids. With simply solvated metal ions this bridging leads to polymeric structure (IV) or possibly (V). In the case of (IV) additional coordination of water, ammonia etc. may occur placing the metal ion in an octahedral environment.

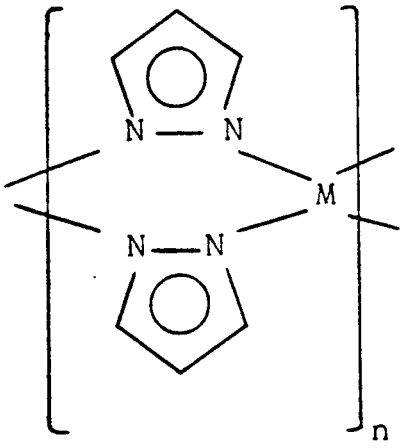


Fig. 4

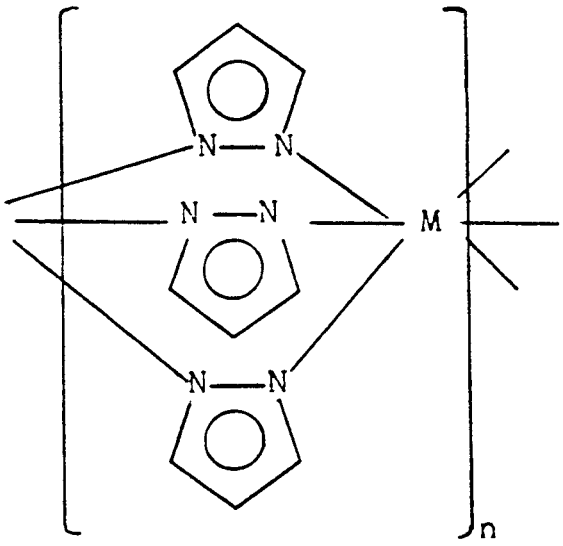


Fig. 5

However, in presence of appropriate encapping groups polymer formation is avoided and monomeric metallocycles have been produced.

Polymeric complexes containing the exobidentate 1,2-di-haptopyrazolide ligand have been known since 1889, when Buchner in his paper on pyrazole reported[37] the formation of the isoluble silver pyrazolides [Ag(Pz)] which he simply denoted as 'silver salt'. The structure of Ag(Pz) has never been established but is probably polymeric $[Ag(Pz)]_n$. An analogous structure has been proposed for $[Cu(Pz)]_n$ prepared from $[Cu(NH_3)_2]^+$ and pyrazolide ion. The mass spectrum show presence of mainly dimers and trimers in vapour, while preliminary X-ray data are compatible with a extended chain structure.

Pyrazolides of many divalent transition metals have been prepared by the reaction of ammonical solution of the metal salts with pyrazole. The polymeric chelates are solvated with water and/or ammonia but may be obtained pure by drying in vacuo[38]. The polymeric pyrazolides are intractable, thermally very stable solids. The $[Cu(Pz)_2]_n$ polymer may be obtained as a brown solid when reaction was performed in ammonia. The brown modification can be converted to green one upon heating with excess pyrazole[39]. Among the various transition metal pyrazolides the most, thoroughly studied one is the insoluble purple cobalt chelate, $[(3,5\text{-}Me_2Pz)_2Co]_n$ which can be precipitated in analytical purity at pH 7.5-9.0. It has been suggested that precipitation of this complex be used for the gravimetric determination of Cobalt[40-41]. Pyrazolides of Fe(II) and Fe(III) have been prepared by the reaction of

pyrazole with a variety of iron derivaties such as $Fe(CO)_5$, $[C_5H_5Fe(CO)_2]_2$ etc.[34]. While air sensitive stable red-brown $[Fe(Pz)_2]_n$ was prepared by either the reaction

$$Ag^{\circ} + [Fe(Pz)_3] \longrightarrow [Fe(Pz)_2]_n + Ag(Pz)$$

or by treatment of $FeCl_3$ with Kpz. Both iron pyrazolide are polymeric and as such insoluble except with decomposition.

There are number of reports on monomeric compounds contain one or more 1,2-dihaptopyrazolide groups bridging to two identical or dissimilar metals or metalloids. The only example of a single bridging pyrazolide ion is the binuclear copper complex (VI) synthsized as the possible model for nitrogen fixing system[42].

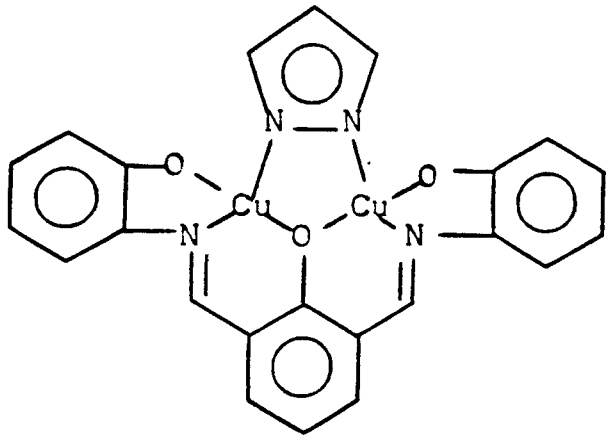


Fig. 6

A variety of metallocycles of the type $[LL'MPz]_2$ (M=Rh, L=CO and L'= 1,5-cyclooctadiene) and Pd (L = π-allyl or 2-substituted π-allyl and L'=1,N-dihapto-2-(diethylaminomethyl) phenyl) containing two 1,2-dihaptopyrazolide (or substituted pyrazolide) bridges have been reported[43]. Molecular models indicate that these metallocycles are not planar but puckered in boat form as confirmed on the basis of the observed n.m.r spectra.

Synthesis and X-ray structures of group 11 pyrazole and pyrazolate complexes have been reported recently[44]. The crystal structure of gold (I) pyrazolate complex; tris [μ-3, 5-bis(trifluoromethyl) pyrazolate-N,N'] tri gold (I) have been reported[45]. However, the structure was not determined accurately due to decomposition, resulting in the formation of small gold particles. The reaction of anhydrous $CuBr_2$ with 3,5-diphenylpyrazole in a 1:2 ratio in THF yielded bis(3,5-diphenylprrazole) dibromocopper(II)[44]. The reaction of $AgNO_3$ in THF with sodium 3,5-diphenylpyrazolate gives tris (μ-3-5, diphenylpyrazolate-N,N') tri-silver(I)[44].

A few pyrazolate complexes with f-block elements have been reported [46-48] where pyrazolate moiety $(Pz)^-$ has bidentate (n^2) bonding (Fig.VII) unlike to that reported[49-51] for d-block transition metals (pyrazolate behave as a bridging ligand). This is a consequence of the non-directional ionic character of f-block metal-ligand bonding[52]. The possibility of π(n^5)

bonding has been considered but not established. The structures of tris (Pyrazolate) lanthanoid (III) complexes, $Ln(Pz)_3$ and their C-substituted derivatives would be of considerable interest, but only one such compound, $Yb(Pz)_3$ has been coniderably studied. $Yb(Pz)_3$ which was obtained by reacting $YbCl_3$ with Na(pz), and was found to be polymeric with either μ-η^2-bonding, η^5-and μ-η^2-bonding, or η^5-and μ-η^5, η^1 bonding.

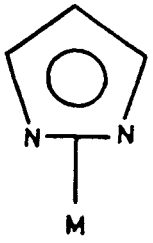


Fig. 7

Recently analogous complexes with bulky, 3,5-dimethylpyrazolate(dmpz) ligand from $LnCl_3$ and Na(dmpz) gave $[Ln_3(\mu\text{-dmpz})_6\ (\eta^2\text{-dmpz})_3\ (\mu_3\text{-O})\ Na_2L_2]$ [Ln=Y, Ho, Yb or Lu; L=H(dmpz) or thf] clusters. However, a reaction of Nd metal with bis (pentaflurorphenyl) mercury and pyrazole (Hpz) or 3,5-dimethylpyrazole (Hdmpz) in THF yielded $Nd(pz)_3$ or $Nd(dmpz)_3thf]_2$. The X-ray crystallographic studies on

$[Nd(dmpz)_3thf]_2$ has revealed a novel centrosymmetric structure with each Nd was found to be eight coordinate (4,4-bicapped trigonial prism) with two terminal chelating dmpz ligands, two bridging dmpz ligands and unexpectedly, two briging THF ligands.

An interesting class of this type of compounds are pyrazoboles[53] that may formally be regarded as composed of two boronium fragments linked by two 1,2-dihaptopyrazolide bridges. The pyrazoboles are prepared by the reaction of a pyrazole with a trialkylborane or borane complex producing symmetrically substituted pyrazoboles[54-56].

$$2Hpz + 2BR_3 \longrightarrow R_2B(pz)_2BR_2 + 2RH$$

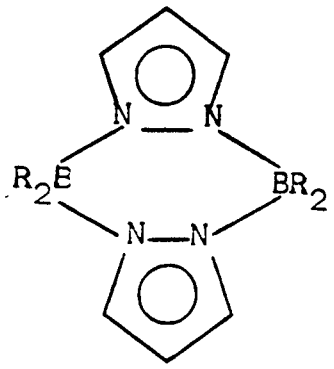


Fig. 8

Pyrazoboles containing different substituents on the two boron atoms are synthesized by the reaction of $[R_2B(pz)_2]^-$ ion

with a borane species containing a leaving group such as halide or sulfonates[57,58].

$$[R_2B(pz)_2]^- + XBR'_2 \longrightarrow R_2B(pz)_2\,BR'_2 + X$$

The tripodal ligand hydrotris (Pyrazol-1-yl)borate, $HBpz)_3$ has been considered as a formal analogue of cyclopentadienide, being a uninegative three electon pair ligand which occupies three coordination sites on a metal. Synthesis of some hydrotris (3,5-dimethylpyrazole-1-yl) borato (aryloxo)zirconium(IV) complexes have been reported[59] recently.

The interaction of pyrazole with heterocycles containing two annular boron atoms generally seems to proceed by initial attack of pyrazole N-H moiety at the most basic site of the heterocycle. The pyrazaboles of the type show in (Fig. IX) have been known for more than three decades.

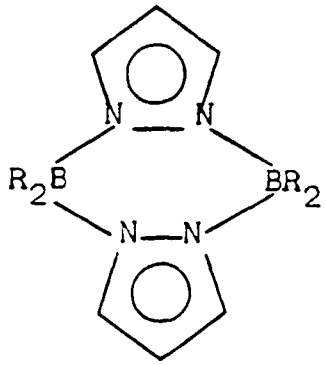


Fig. 9

Triple bridged pyrazaboles were discovered[60,61] recently. The compound of the type shown in (Fig. X) were obtained from the reaction of borazines $-(RBNR')-_3$ with pyrazoles and three such species (X=NHR') have been reported[62] only most recently, four additional species containing the central B_2N_2X ring of structure have been obtained from the reaction of bis(diorganoboryl) chalcogenides, $(R_2B)_2X$

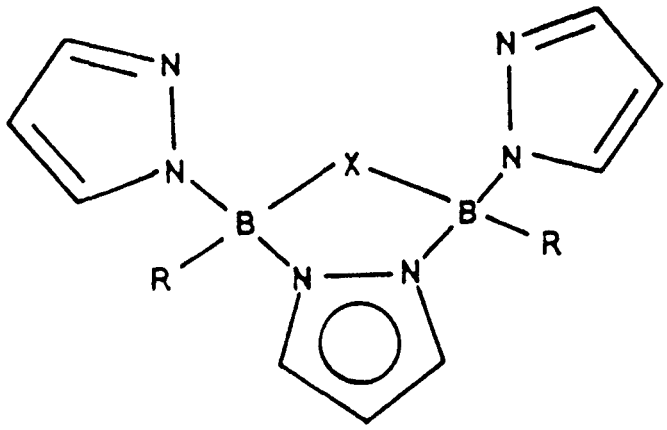


Fig. 10

($R=C_2H_5$, X=O; R_2 =1,5-C_8H_{14}; X=O or S or Se) with pyrazole[62], Other variations of are the low temperature dimerization products of 1-pyrazolyboranes containing trigonal boron[44] as well as addition of the latter with monoaminoboranes[44], however it was found that such compounds are stable only at low temperature[63,64].

Coordination compounds of sulfur with transition metal ions have assumed importance in the recent[65] years owing to their application in medicine, agriculture and industry. The palladium and platinum complexes of 6-mercaptopurine are known to destroy adenocarcinomas. Thiazoles and 2-methylbenzo thiazole complexes are being studied[66] because of their importance in biological systems. Certain metal complexes of thiazoles and imidazole thiol have been used as antioxidants and heat resistant materials[67,68] in addition to acting as fungicides and insecticides. Thiocarbohydrazide are useful in many important anticarcinogenic and antibacterial properties[69].

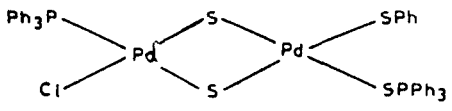
The metallothioneins constitue a unique class of metalloproteins which are polymetallic with exclusive coordination by a cysteine thiolate function[70,71]. The best characterized metallothioneins contains seven metal atoms (Zn and/or Cd) of cysteinate side chains, and are devoid of aromatic aminoacids[72]. All cysteinate groups are metal bound, some as bridging ligands probably in aggregates with three and four metal atoms[73-77]. The metals Zn, Cd, Hg, Cu, Ag and Pb induce the formation of metallothioneins and can be involved in their probable functions of metal storage and metal detoxification by sequestration[78].

Several monomeric nickel, palladium and platinum thiolato-complexes are known with coordinated tertiary

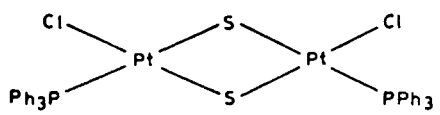
phosphine and arsines[79]. The four coordinate species $[Ni(SR)_2(PR_3)_2]$ have been synthesized by metathesis of sodium-alkanethiolate with $[NiCl_2(PR_3)_2]$. The analogous palladium complexes are prepared similarly but they are square planar and dissociate to some degree in solution[80].

A great deal of the chemisry of metal thiolates involves thiolates as a bridging ligand. Thiolates can bridge between two or three metal to give dinuclear, linear or three dimensional cluster compounds of high polymers and the bridges can consists of one, two, three or four thiolate sulphur atoms[79].

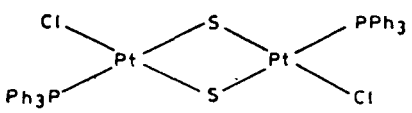
The synthesis of di-μ-SR bridged palladium species $[Pd(SPh)_2 (PPh_3)_2 I_2]$ (A) have been reported[81] by treatment of polymeric $[Pd(SPh)_2]_n$ with triphenylphosphine or by oxidative-addition of RSSR to $[Pd(PPh_3)_4]$[82] and similar complexes $[(Pt(PR_3) Cl(SR)_2]$ are known in which the chloride ligands are terminal[83]. In the last complexes it was found that the Cis-isomer(B) were more stable than the trans-isomer(C).



[A]



[B]



[C]

The dinuclear species $[Au_2(SC_6F_5)_6]^{-2}$ has been reported[84] and characterized and appears to have a doubly thiolate-bridged structure.

Discrete complexes with triple thiolate bridges are confined almost exclusively to those containing iron, molybdenum and or tungesten. In many cases the triple bridge is supported by a metal-metal bond[85]. The complex cation, $[(Cd(SCH_2CH_2NH_2)_3)_2M]^{3+}$ (M=Fe or Ru) has been confirmed by EPR spectroscopy[86]. Virtually all the complexes with quadruple thiolate bridges have π-cyclopentadienyl or π-arene terminal ligand[87]. The first reported complex of this type was $[(CpV)_2(M\text{-}SMe)_4]$ which has been found to show a low magnetic moment suggesting strong magnetic exchange through the sulfur bridges or possibly via a direct metal-metal interaction[88].

A wide variety of synthetic methods have been used for incorporation of thiolate into transition metal complexes. The simplest and most direct method involve the displacement of halideion by thiolate anion, which has an advantage over the use of RSH. One of the principal factors governing the reactivity of thiolate complex is the availability of electron density on the sulfur atoms which encourages attack by electrophiles at the sulfur atom of thiolate complexes[79]. The thiolate substitution reaction in the iron-molybdenum sulfur cubane clusters are dependent on nucleophilic and on basic properties of the coordinated thiolate making use of

protonation and acylation by thiol and acyl halide[89]. As indicated by this type of reactivity, the availability of electron density at the sulfur atom is much greater than at the oxygen atoms of analogous alkoxide complexes[79].

The synthesis and applications of the macrocyclic moieties involving N,P, O and S atoms in the ring could be a subject of considerable interest in the recent years. The chemistry of these macrocyclic system is expanding rapidly which is mainly confined to systems containing N, O, P, and S donor atoms with little attention to P and As containing macroycycles.

While searching the literature it is being disclosed that several references of cyclic polyethers containing four or more oxygen atoms in the polyether ring. Luttringhaus and Zeigler prepared cyclic polyethers derived from resorcinol[90] While Adams and whitehill prepared from hydroquinone[91]. A compre hensive review dealing with of crown ethers synthesis has been published by Gokel and Korzeniowsks[92].

Now a number of efficient methods are available for the synthesis of various polyether and polythiomacrocycles[92-99]. The reaction are sometimes aided by metal template assistance[100,101]. The size of the macrocyles depend upon the reaction conditions.

The chemistry of alkali and alkaline earth metal

cations expanded greatly with the discovery of the binding properties of natural macrocyclic antibiotics[102] of crown ether in 1967. Actinides and Lanthanides have not been studied as extensively as the transition metals, although they forms complexes with cryptands as well as other macrocyclic ligands[103,104].

The synthesis of phosphorus macrocycle is difficult because of the experimental difficulties and hazards of phosphorus (III) chemistry. The phosphorus macrocycles are made via template condensation of coordinated polyphosphine ligands and a dibromoalkane[105,106]. Russian workers[107,108] have synthesized a series of phosphorus containing crown utilizing O-P-O bonds in the macrocycles.

Aza macrocyclic ligands are important because of its biological importance. The systematic development of macrocyclic chemistry started in the year 1960 with the pioneering work of D.H. Busch. Mostly macrocyclic ligands have been developed from two biological archetypes. The first porphyrins are best examplified by haemin. The second group were modelled are valinomycine[109] which was shown to be capable of transporting metals trough biological membrane. Considration to this system led to the development of macrocyclic polyethers[110].

The macrocyclic ligands have variety of applications extending the range and scope of coordination chemistry[111,112]

which may act as models for naturally occuring metalloprotein systems[113-115]. It lead to the researchers to begin with the study of the synthesis, reactivity and the coordinating behaviour of these macrocyclic ligands.

Azamacrocyclic compounds are prepared by three types of procedures :

(i) Conventional organic synthesis of the ligands.

(ii) Metal ion promoted reaction involving condensation of non-cyclic components in presence of suitable metal ion.

(iii) Modification of the compounds prepared by procedure (i) and (ii).

A great variety of aza macrocyclic complexes have been formed by condensation reaction in the presence of metal ions. The majority of such reactions have imine formation as the ring closing step. Fourteen [14] and to a lesser extent, sixteen [16] membered tetraaza macrocycles predominate and nickel (II) and copper (II) are the most active metal ions involved in it.

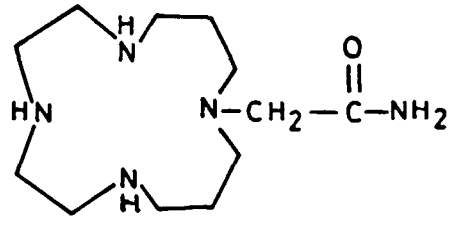


Fig. 11

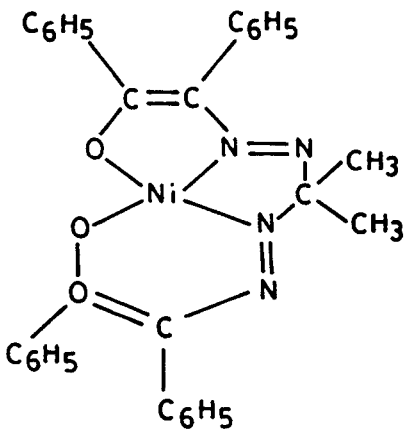


Fig. 12

Condensation of diamine with dicarbonyl compounds is a source of imino macrocycles. For aliphatic diamines the reactivity is sufficiently enhanced by a variety of substituent at the 2-position of the 1,3-dicarbonyl compound e.g; acyl, bromo, diazophenyl etc.

Condensation of a monocarbonyl compound with a dihydrazone have been reported. Tetradentate and Pentadentate azamacrocycles are formed by condensation of 2,6-diacetyl pyridine with hydrazine or with dihydrazine[116]. However, Bora substituted azamacrocycles are formed by reaction of oxime complexes with boron compounds have also been reported.

The properties of the azamacrocyclic compounds generally resembles with those of their non-cyclic analogous. The metal ions have some catalytic or 'template' activity in the formation of such macrocyclic ligands[117, 118].

Survey of literature reveals that multidentate macrocyclic ligands containing N and O atoms are cyclic molecules consisting of an organic frame work interspread with hetro atoms which are capable of interacting with a variety of species.

Hard donor atoms N and O provide the binding sites such as RCO_2^-, RO^-, ROR and R_3N for hard or intermediate acid. The soft donor atoms P, As and S potentially act as stablizing influence to the more polarizable substrate. These hetro atoms have been studied scarcely in comparison to the N and O atoms containing analogs. Where as thioether macrocycles are amongst the most throughly studied and chracterized macrocycles with first row as well as heaviar trnsition metals[119].

The interaction of metal ions with O and N donor macrocycles involved synthetic, kinetic, thermodynamic and structural aspects of complex formation with a range of transition metal ions and heavy metal ions[120-122].

Condensation reaction between dicarbonyl compounds and primary diamines provide a synthetic route for the preparation

of macrocyclic ligands[123, 124]. Usually such synthesis are carried out in the presence of a suitable metal ion which serve to direct the steric course of reaction preferentially towards the cyclic rather than oligomeric/polymeric products.

Several designs and systhesis of polyazamacrocycles bearing flexible pendant arms from the cyclic frame work which provides additional coordination sites have attracted considrable interest in recent years. The possible relevance of these macrocyclic compounds as model ligands for metal enzymes and metal-protein are useful in general co-ordination chemistry[125].

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CHAPTER - II
EXPERIMENTAL METHODS

EXPERIMENTAL METHODS

There are several physico-chemical methods available for the study of coordination compounds. A brief description of the techniques used in the investigation of the newly synthesized complexes described in the present work are given below :

1. Infrared Spectroscopy
2. Nuclear Magnetic Resonance Spectroscopy
3. Magnetic Susceptibility Measurements
4. Ultraviolet and visible (Ligand Field) Spectroscopy
5. Conductometry and
6. Elemental Analysis

Infrared Spectroscopy

Infrared absorption spectra are commonly obtained by placing the sample in one beam of a double beam infra red spectrophotometer measuring the relative intensity of transmitted and therefore the absorbed light energy versus wave number when the infra red light of the same frequency is incident on the molecule, energy is absorbed and amplitude of that vibration is measured. When the molecule reverse from the excited state to the original ground state, the absorbed energy is released as heat. The occurrence or non-occurrence of an infra red radiation is governed by the following selection rules.

(i) In order for a molecule to absorb infra red radiation as

vibrational excitation energy, there must be a change in the dipole moment of the molecule as it vibrates.

(ii) In the absorption of the radiation, only transition for which change in the vibrational energy level is V = 1 can occur, since most of the transition will occur from state V_0 to V_1, the frequency corresponding to this energy is called the fundamental frequency.

The frequency of certain groups of atoms is called group frequency. These frequencies are characteristic of the group irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the appropriate region indicates the absence of that particular group in the molecule.

The infra red region and the electromagnetic radiations covers a wide range of wave lengths lying between 0.8 μ to 1000μ. The wave number i.e. the number of waves per centimeter is used to characterize the radiation.

The infra red region has been classified in the following paragraphs, only those frequencies which are pertinent to the discussion of the newly synthesized compound are discussed below :

N-H Stretching Frequency

The N-H stretching vibrations occur in the region[1] 3500-

3300 cm^{-1} in dilute solution. The N-H stretching band shifts at lower value in the solid state due to extensive hydrogen bonding. Primary amines in dilute solutions, in nonpolar solvents give two absorption bands in the above mentioned region, the first of which due to symmetric stretch is usually found near 3500 cm^{-1} and second which corresponds to asymmetrical mode is found near 3400 cm^{-1}. These bands are usually 125-150 cm^{-1} apart from each other. Secondary amines show only a single N-H stretching in dilute solutions. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3350-3310 cm^{-1} (low intensity) in aliphatic, secondry amines and near 3490 cm^{-1} (much higher intensity) in heterocyclic secondary amines such as pyrozole and imadazole.

The N-H (Pyrrolic) stretching vibration appear at a lower wave length 2920 cm^{-1} which is attributed to intra and intermolecular hydrogen bonding. The N-H bending vibrations have been reported for many solid pyrazole.

C=N Stretching Frequency

A medium intensity band has been reported to appear at 1490 cm^{-1} characteristic of C=N stretching[2] vibration in pyrazoles. However, it undergoes a negative shift of about 10-30 cm^{-1} on coordination to the metal ions.

C≡N Stretching Frequency

There has been a number of reports for coordination of CN group through nitrogen and a strong band has been observed at 2250 cm^{-1} for a free CN group. However, a positive shift (15-35 cm^{-1}) in C ≡N stretching vibration suggest a coordination of CN group through nitrogen.

S-H Stretching Frequency

The S-H stretching vibrations in mercaptans are usually observed in the range 2600-2500 cm^{-1} [2]. The S-H absorption is not inherently strong, and is often difficult to detect in dilute solution or in samples examined in very thin cells.

NH_2 Group Vibration

A multiplet (two to three medium to strong intensity bands) generally in the region 3300-3400 cm^{-1} correspond to NH str. vibration in primary amines. However, the bands in the range 1580-1620 cm^{-1} are reported for NH_2 deformation modes and the weak intensity bands in 1300-1360 cm^{-1} region corresponds to NH_2 Wagging and rocking.

C-O Stretching Vibration

A strong band has been obtained in i.r. spectra of primary alcohols 1010-1075 cm^{-1} characteristic of C-O str. mode. However, the same band has been reported to appear at 1105-1120 cm^{-1} for secondary alcohols.

Alkoxide-O-R [R = CH_3, C_2H_5] Stretching modes

A strong band ~1030 cm^{-1} is associated with a bridging alkoxide group. However, a band at 1060 cm^{-1} corresponds to terminal alkoxide group in metal alkoxides.

M-N Stretching Frequency

The M-N stretching frequency is of particular interest since it provides direct information regarding the coordinate bond. A preliminary investigation of the infra red spectra of pyridine complexes in 200-500 cm^{-1} region located bands which were assigned to M-N str. vibrations[3]. Complexes exhibited the metal-nitrogen stretching frequency in the region 300-420cm^{-1}.

M-Cl Stretching Vibrations

The halogens are the most common ligands in the coordination chemistry. The MX str. vibration is the direct evidence for halogen coordination. The terminal M-Cl str. band appear in the region 200-300 cm^{-1} which depends on the oxidation state of the metal. However, the bridging M-Cl str. frequencies normally appearing in the region 152-300 cm^{-1}.

M-P Stretching Frequency

Triphenylphosphine is most common phosphorous ligand. It is not simple, however, to assign the M-P str. frequency of PPh_3 in complexes since PPh_3 exhibit a number of ligand vibrations in the low frequency regions. Nakamoto[4] et al showed that the i.r. spectrum of tetrahedral $Ni(PPh_3)_2Cl_2$

exhibit ν Ni-P bands at 1896 and 164 cm^{-1} confirmed on the basis of using metal isotope techniques. The i.r. spectrum of $[Ni\text{-}Ph_3]CO_3$[5], $Ni(Ph_3)_4$[6] and $Ni(Ph_3)(PF_3)_3$[7] exhibit Ni-P str. mode in the range 295-340 cm^{-1}.

M-S Stretching Frequency

The metal sulphur stretching frequency is of particular interest as it gives a direct evidence for coordination through the sulphur atom. In thiophenolyl borates the metal-sulphur stretching frequency[8] has been located as a weak aborption band in the region 390-340 cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy

The nuclei of certain isotopes possess a mechanical spin or angular momentum. The total angular momentum depends on the nuclear spin or spin quantum number I which may have the values 0, 1/2, 3/2 ..... (depending on the particular nucleus). The n.m.r. spectroscopy is most often concerned with nuclei having I = 1/2, examples of which includes ^{1}H, ^{31}P, ^{19}F.

For a nucleus with I = 1/2 there are two values for the nuclear spin angular momentum quantum number m_I viz., + 1/2 and -1/2 which in the absence of a magnetic field are degenerate. In presence of mangnetic field however, this degeneracy is destroyed such that the positive value of m_I corresponds to the lower energy state and the negative value to higher, separated by E. A nucleus with a mangetic moment

can be visualized as bar magnet which spins on its axis. The magnetic moment interacts with the external field when the nucleus is placed in it and produces torque. This torque interacts with the angular momentum and causes magnetic moment to precess about the applied field vector, Ho. The angular frequency , of the precession is referred to an Larmor frequency whose magnitude is determined by the expression given below :

$$\omega = \gamma Ho$$

The quantity γ (radians gauss^{-1} sec^{-1}) referred to as the magnetogyric ratio, is a constant for a given nucleus.

In an n.m.r. experiment one applied strong homogeneous magnetic field causing the nuclei to precess. Radiation of energy comparable to ΔE is then imposed with a radio frequency transmitter is equal to the Larmor frequency the two are said to be in 'resonance' and the energy can be transferred to and from the source and the sample and n.m.r. signal is obtained when a nucleus is excited from the low energy to the high energy state. The Larmor frequency is generally matched with a fixed radio frequency by varying the field strength Ho.

The magnitude of the field seen at the nucleus, H_N is different from the applied field Ho due to shielding by electrons and is given by the relation.

$$H_N = Ho(1-\sigma)$$

Where σ is a constant representing the shielding of the nucleus by the electrons. An accurate measurements of H_N and Ho is very difficult. Instead a reference material is employed and the difference in the field strength Hs at which the sample nucleus absorbs and H_R at which the nucleus in the reference compound absorbs is measured. The chemical shift ò which is independent of the field strength is defined as

$$\delta = \frac{\Delta\nu \times 10^6}{\text{fixed frequency of the probe}}$$

Where $\Delta\nu$ is the difference in the absorption frequencies of the sample and reference in cps, the fixed frequency or the oscillator frequency is characteristic of the instrument. A 60 Mc instrument has an oscillator frequency of 60×10^6 cps. The factor ò is a dimensionless quantity expressed in parts per million (ppm).

The fine structures of the n.m.r. peaks due to various nuclei arises from the phenomenon known as spin-spin splitting. The separation J (usually expressed in cycles per second) between the peaks comprising the fine structure is referred to as the spin-spin coupling constant. The number of peaks in the fine structure of the spectrum due to an atom A

being split by a non-equivalent atom B is given by the following formula :

$$n = 2\Sigma S_B + 1$$

Where ΣS_B is the sum of the spins of equivalent B nuclei. The relative intensities of the peaks can be obtained from the coefficients of the terms that results from the binomial expansion $(1+x)^m$, where $m = n-1$.

The spin-spin splitting pattern and characteristic J value provide extremely useful information regarding the structure of the species being investigated.

Experimental Techniques

^1H n.m.r. spectra were determined in DMSO using a Bruker WM 250 Fourier-tranform instrument with TMS as internal standard.

Magnetic Susceptibility Measurement

The determination of magnetic moments of transition metal complexes have been found to provide ample information in assigning their structure. The main contribution to bulk magnetic properties arises from magnetic moment resulting from the motion of electrons. It is possible to calculate the magnetic moments of known compounds from the measured values of magnetic susceptibility.

There are several kinds of magnetism in substances viz., diamagnetism, paramagnetism and ferromagnetism or antiferromagnetism. Most compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the closed shell electrons with an applied mangetic field. In the closed shell the electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighbouring atoms.

If a substance is placed in a magnetic field H, the magnetic induction B with the substance is given by

$$B = H + 4\pi I$$

Where I is the intensity of magnetisation. The ratio B/H is called the mangetic permeability of the material and is given by :

$$B/H = 1 + 4\pi(I/H) = 1 + 4\pi K$$

Where K is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of density of lines of force within the substance to the density of such lines in the same region in the absence of the sample. Thus the volume susceptibility of a vacuum is by definition zero since in vacuum B/H = 1.

When magnetic susceptibility is considered on the weight

basis, the gram susceptibility (χ_g) is used instead of volume susceptibility. The μeff value can then be calculated from the gram susceptibility multiplied by the molecular weight and corrected for diamagnetic value as

$$\mu_{eff} = 2.84 \sqrt{\chi.M^{corr} \quad T.} \quad B.M.$$

Where T is the absolute temperature at which the experiment is performed.

The magnetic properties of any individual atom or ion will result from some combination of these two properties that is the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus. The magnetic moments are usually expressed in Bohr magnetons (B.M). The magnetic moment of a single electron is given by

$$\mu_S \text{ (in B.M.)} = g \sqrt{S(S+1)}$$

Where S is the spin quantum number and g is the gyromagnetic ratio.

For Mn^{2+} and Fe^{3+} and other ions whose ground state terms are 'S', there is no orbital angular momentum. In general however, the transition metal ions in their ground state D or F being most common, do possess oribtal angular momentum. For such ions, as Co^{2+} and Ni^{2+}, the magnetic moment is given by

$$\mu \; S + L = g \sqrt{4S(S+1) + L \; (L+1)}$$

in which L represnts the orbital angular momentum quantum number for the ion.

The spin magnetic moment is insensitive to environment of metal ion, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and there by an orbital magnetic moment with reference to a given axis it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis.

Electrons in d states cannot contribute to the orbital moment because the d_x2-y2 and d_z2 orbitals cannot be transformed into one another by a rotation about any axis. However, all dE states excepting d^3 and d^6 contribute to the orbital moment.

For octahedral complexes the orbital angular momentum is absent for A_{1g}, A_{2g} and E_g term, but can be present for T_{1g} and T_{2g} terms. Magnetic moments of the complex ions with A_{2g} and E_g ground terms may depart from the spin only value by a small amount. The magnetic moments of the complexes possessing T ground terms usually differ from the high spin value and vary with temperature. The magnetic moments of the complexes having a $^6A_{1g}$ ground term are very close to the spin only value and are independent of temperature.

For octahedral and tetrahedral complexes in which spin-orbit coupling causes a split in the ground state, an orbital

moment contribution is expected. Even no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with higher states can appear due to spin-orbit coupling giving an orbital moment contribution.

Practically the magnetic moment value of the unknown complex is obntained on Gouy magnetic balance. Farady method can also be applied for the magnetic susceptibility meaurement of small quantity of solid samples. The magnetic moments of the most of the present compounds was carried out on Faraday balance.

Ultra-violet and Visible (Ligand Fields) Spectroscopy

Most of the compounds absorb light somewhere in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal all the five 'd orbitals' viz. d_{xy}, d_{yz}, d_{xz}, d_z and d_x2-_y2 are degenerate. However, in coordination compounds due to the presence of ligands this degeneracy is lifted and d orbitals split into two groups called t_{2g} (d_{xy}, d_{yz} and d_{xz}) and e_g (d_z2 and d_x2-_y2) in an octanhedral complex and t and e in a tetrahedral complex. The set of t_{2g} orbitals goes below and the set of e_g orbitals goes above the original level of the degenerate orbitals in an octahedral complex. In case of the tetrahedral complexes the position of the two sets of orbitals is reversed the 'e' going below and 't' going above

the original degenerate level when a molecule absorbs radiation its energy equal in magnitude to hνand expressed by the relation,

$$E = h\nu$$

or

$$E = hc/\lambda$$

Where h is planck's constant ν and λ are the frequency and wavelength of the radiation respectively and C is the velocity of light.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon 'Russell-Saunder Scheme' must be introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as 'Term Symbols'.

The orbital angular momentum of electrons in a filled shell vectorocally add upto zero. The total orbital angular momentum of an incompleted shell electron is obtained by adding L value of the individual electrons, which are treated as a vector with the component ml in the direction of the applied field. Thus

$$L = \Sigma_i \; ml \quad i = \begin{array}{ccccccc} 0 & 1 & 2 & 3 & 4 & 5 & 6 \\ S & P & D & F & G & H & I \end{array}$$

The total spin angular momentum $S = \Sigma_i s_i$ where s_i is the value

of spin angular momentum of individual electrons. S has a degeneracy T equal to 2S+1, which is also known as 'Spin Multiplicity'. Thus a term is finally denoted as 'TL'. For example, if S = 1 and L = 1 the term will be ^3p and similarly if S = 1½ and L = 3, the term will ^4F.

In general the terms arising from a d^n configuration are as follows :

d^1 d^9 : ^2D

d^2 d^8 : ^3F, ^3P, ^1G, ^1D, ^1S

d^3 d^7 : ^4F, ^4P, ^2H, ^2G, ^2F, $^2D(2)$, ^2P,

d^4 d^6 : ^5D, ^3H, ^3G, $^3F(2)$, ^3D, $^2P(2)$, ^1I, $^1G(2)$, ^1F, $^1D(2)$, $^1S(2)$

d^5 : ^4S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $^2G(2)$, $^2F(2)$, $^2D(3)$, ^2P, ^2S,

Coupling of L and S also occurs, because both L and S if non-zero, generate magnetic fields and thus tend to orient their moments with respect to each other in the direction where their interaction-energy is least. This coupling is known as 'LS coupling' and gives rise to the resultant angular momentum denoted by the quantum number J which may have quantized positive values from [L + S] upto [L - S] e.g. in case of ^3p (L=1, S=1), ^4F (L=3, S=1½) possible values of J representing state, arising from term splitting are 2,1 and 0

and 4½, 3½, 2½, and 1½. Each state specified by J is 2J+1 fold degenerate. The total number of states obtained from a term is called the multiplet and each value of J associated with a given value of L is called component. Spectral transitions due to spin orbit coupling in an atom or ion occurs between the components of two different multiplets while LS coupling scheme is used for the elements having atomic number less than 30, in whose case spin orbit interactions are large and electrons repulsion parameters decrease. The spin angular momentum of an individual electron couples with its orbital momentum to give an individual J for that electron. The individual J's couple to produce a resultant J for the atom. The electronic transitions taking place in an atom or ion are governed by certain 'Selection Rules" which are as follows:

1. Transitions between states of different multiplicity are forbidden.

2. Transitions involving the excitation of more than one electron are forbidden.

3. In a molecule, which has a centre of symmetry, transition between two gerade or two ungerade state are forbidden.

Inter-electron repulsions within configuration give the energies of the terms above the ground term.

The energies are function of two parameters related to electron repulsion. The two parameters may be choosen in either the way of Condon and Shortley (F_2 and F_4) or in that of Racah (B and C) for d orbital electrons. For the first transition series ions the value of C/B is around 4.0 and B is about 1000 cm^{-1}. It is possible to examine the effects of crystal field on a polyelectron configuration. The ligand field splitting due to cubic field can be obtained by consideration of group theory. It has been shown that as S state remains unchanged. P states does not split, a D state splits into two and F state into three and a G state into four states are tabulated below. This holds for an octahedral 'Oh' as well as tetrahedral 'Td' symmetry.

S ——————— A_1

P ——————— T_1

D ——————— $E + T_2$

F ——————— $A_2 + T_1 + T_2$

G ——————— $A_2 + E + T_1 + T_2$

In weak crystal fields the inter-electron repulsions are larger. The crystal-field may be however be of comparable magnitude (medium strength) or it may be larger than the inter-electron repulsion.

The correlation diagram for free ion (weak-field) ⟶ (strong-field) configuration from d^1 - d^9 for both octahedral and tetrahedral cases are available. In addition to the

qualitative aspects of transition from weak to strong crystal-fields it is also necessary to have quantitative results availabel for the interpretation of the spectra. The so called Tanabe-Sugano diagrams make it possible. In these diagrams, the energies of the levels of a d^n system as E/B are plotted as the vertical coordinate and the crystal field strength in the form of D_q/B as the horizental coordinate. This diagram requires two parameters B and C for the inter-electron repulsion. It can be drawn only if the ratio C/B is specified.

Transition from the ground state to the excited state occur according to selection rules described earlier. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse of that for this ion in a tetrahedral field.

Sometimes due to transfer of charge from ligand to metal or metal to ligand, band appear in the ultra-violet region of the spectrum. Such spectra are known as 'charge transfer spectra' or redox spectra. For metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transition. However, these should be clearly discerned from the ligand bands which might also occur in the same region.

Conductometry

The conductivity measurements is one of the simplest and easily available techniques, used for characterization of compounds. It gives direct information regarding wheather a given compound is ionic or covalent. For this purpose the measurement of molar conductance (Λ_m) which is related to the conductance value in the following manner :

$$\Lambda_m = \frac{\text{Cell constant x conductance}}{\text{concentration of solute expressed in moles } cm^{-3}}$$

Conventially solutions of 10^{-3}M strength are used for the conductance measurment. Molar conductance values of different types of electrolytes in the solvents are given below :

A 1 : 1 electrolyte may have a value of 75-95 Ohm^{-1} cm^2 mol^{-1} in nitromethane, 50-75 Ohm^{-1} cm^{-2} mol^{-1} in dimethyl suplhoxide, 72-90 Ohm^{-1} cm^2 mol^{-1} in dimethyl formamide and 100-160 Ohm^{-1} cm^2 mol^{-1} in methyl cyanide. Similarly a solution of 2:1 electrolyte may have m value of 150-180 Ohm^{-1} cm^2 mol^{-1} in nitromethane, 130-170 Ohm^{-1} cm^2 mol^{-1} in dimethyl formide and 140-220 Ohm^{-1} cm^2 mol^{-1} in dimethyl sulphoxide.

Elemental Analysis

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. Carbon, hydrogen and nitrogen analyses were obtained from micro-analytical laboratory of I.I.T., Delhi and

C.D.R.I. Lucknow (India). Sulfur and chlorine were analysed by conventional methods by decomposing a known amount of the sample in a platinum crucible which was latter dissolved in water using a little amount of concentrated hydrochloric and nitric acid respectively. For the metal estimation , a known amount of complex was decomposed with a mixture of nitric, perchloric and sulphuric acids in a beaker. It was then dissolved in water and made upto a known volume so as to titrate it with standard EDTA. The solution was then treated with either barium sulphate or silver nitrate solution. The precipitate was dried and weighed.

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CHAPTER - III

SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON THE COMPLEXES OF FIRST ROW TRANSITION METAL CHLORIDES AND GROUP IIB METAL CHLORIDE AND THEIR TRIPHENYL PHOSPHINE DERIVATIVES WITH 4-CYANO-5-AMINOPYRAZOLE.

INTRODUCTION

The coordination chemistry of pyrazole and substituted pyrazoles has been exhaustively studied and a variety of complexes of 2-monohaptopyrazoles, Rpz (R =H,Me, Ph) (I) with metals and metalloids[1-5] have been prepared. The coordination has been reported via pyrazole nitrogen N(2) of the five membered ring based on different physico-chemical methods. This has been further confirmed by X-ray crystallography[6-10]. However, the number of pyrazoles coordinated to a metal ion is influenced by coordinating ability of the counter ion[1,5], the nature of the metal ion[1,3,11,12] and substitution on the pyrazole ring[3,13]. The complexes of substituted pyrazoles viz., 3,5-dimethylpyrazole, H3,5Me_2Pz, 4-methylpyrazole, H4MePz, 3-methyl-5phenylpyrazole, H3Me5Phpz and 3-methyl-5-aminopyrazole, H3Me5NH_2pz with a variety of transition metal ions have been reported[14] to bond via pyrazole N(2) except the complex of PhMeNH_2pz with trialkylboranes which has been found to be coordinated by NH_2 group. In this chapter we describe the coordinating behaviour of the substituted pyrazole having two strong donor groups i.e. 4-cyano-5-aminopyrazole, H4CN5NH_2pz with anhydrous divalent transition metals chlorides and their triphenylphosphine derivatives in order to investigate if N(2) still coordinate to metal ions in the presence of these two strong donor groups.

EXPERIMENTAL

Material and Methods

The reagents, triphenylphosphine (Sisco), $CrCl_2$, $6H_2O$, $FeCl_2.6H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2$ and $HgCl_2$ (all BDH) were commercially pure samples. The ligand 4-cyano-5-aminopyrazole was prepared by reported method[15]. The purity of the ligand was checked by microanalysis, M.Pt. and spectral studies.

Solvents tetrahydrofuran, dimethylsulphoxide and ethanol (all E.Merck) were commercially pure samples and were dried before use by literature procedure[16].

Dehydration[17] of hydrated transition metal chlorides;$MCl_2.nH_2O$ [M =Cr, Mn, Fe, Co, Ni for n =6; Mn for n = 4; Cu for n = 2]

10 grams of hydrated metal (II) chlorides were seperately taken in a round bottom flask and covered with 50 cm^3 of thionyl chloride. The contents were refluxed for 2 hrs. The excess $SOCl_2$ was removed by distillation. The $SOCl_2$ which clings to the solid compounds was removed by repeated washing with dry Et_2O and vacuum dried in a closed filteration frit.

Preparation[18] of Dichlorobis (triphenylphosphine) Mn(II)

1.9 gm (10 m mol) of anhydrous $MnCl_2$ was dissolved in dry tetrahydrofuran followed by the addition of 5.25 gm (20 m mol) of triphenylphosphine. The reaction mixture was refluxed for 3

hrs. The final product was then precipitated by adding Et_2O and then filtered and dried [M.Pt. 232°C].

Preparation[19] of Dichlorobis (triphenylphosphine) Co(II)

An excess of triphenylphosphine 2.62 gm, (10 m mol) was melted on a water bath followed by the addition of $CoCl_2.6H_2O$ 1.92 gm (5 m mol) with continuous magnetic stirring for 5-10 minutes. . The reaction mixture was thereafter cooled and grind in a mortar. The blue product obtained was recrystallized from hot ethanol. [M.Pt. 225°C].

Preparation[20] of Dichlorobis(triphenylphosphine) Ni(II)

A solution of $NiCl_2.6H_2O$, 1.19 gm, (5 m mol) in water was diluted with 25 cm^3 glacial acetic acid and triphenyl-phosphine 2.62 gm, (10 m mol) in 50 cm^3 glacial acetic acid was added. The olive green microcrystalline mass precipitated out, when kept in contact with its mother liquor for 24 hrs. resulting in the formation of dark blue crystalline solid which was filtered off, washed with glacial acetic acid and dried in vacuum [M.Pt. 244°C].

Preparation[21] of Dichlorobis(triphenylphosphine) Zn(II)

The solution of anhydrous $ZnCl_2$ 0.6814 gm, (2.5 m mol) in ether was added to the triphenylphosphine solution in dry benzene 2.62 gm (10 m mol) resulting in the slow precipitation of white crystalline solid [M.Pt. 336°C].

Preparation[21] of Dichlorobis (triphenylphosphine) Hg(II)

1.1gm, (2 m mol) triphenylphosphine disolved in 50 cm^3 hot ethanol and mercuric chloride 0.5 gm, (1m mol) in 25 cm^3 of hot ethanol was rapidly mixed and allowed to cool. White crystals of the dichlorobis (triphenylphosphine) mercury (II) were filtered off and dried in vacuum [M.Pt. 273°C].

Preparation[22] of Dichlorobis(triphenylphosphine) Cd(II)

Triphenylphosphine 10 gm (2 m mol) and solution of cadmium chloride 15 gm (1 m mol) in water (15 cm^3) were vigorously shaken together giving rise to the crystalline precipitate which was filtered and dried in vacuum. This was recrystallized from ethanol [M.Pt. 134°C].

Reaction of $H4CN5NH_2pz$ with anhydrous metal chlorides, MCl_2. Synthesis of Dichlorotetrakis 4-cyano-5-aminopyrazole) Metal (II) complexes ML_4Cl_2 [M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II)].

The stoichiometric amounts of metal (II) chlorides in THF were separately reacted with slightly excess amount of ligands 4-cyano-5-aminopyrazole taken in hot ethanol as described in the following paragraph.

Dichlorotetrakis(4-Cyano-5-aminopyrazole)Cr (II):

$[Cr(C_{16}H_{16}N_{16})Cl_2]$(1a)

To a 0.045 mol of ligand dissolved in hot ethanol 0.01

mol chromium (II) chloride in 50 cm^3 of THF was slowly added at room temperature. The reaction mixture was stirred for 3 hrs under dry N_2 atmosphere. A light green amorphous solid was obtained on prolonged magnetic stirring. The solid thus formed was filtered, washed several times with EtOH followed by Et_2O and dried in vaccum [Yeild 68%, M.Pt. 353°C].

Dichlorotetrakis (4-Cyano-5-aminopyyrazole) Mn(II), [Mn[$(C_{16}H_{16}N_{16})Cl_2$] (2a)

0.02 mol of anhydrous $MnCl_2$ solution in THF was added slowly to ligand (0.05 mol) solution in hot ethanol at room temperature followed by magnetic stirring for 3 hrs under dry N_2 atmosphere resulting in the isolation of colourless solid product. The product thus formed was filtered off, washed several times with EtOH and finally with Et_2O and dried in vacuum. [Yeild 70%, M.Pt. 340°C].

Dichlorotetrakis (4-Cyano-5-aminopyyrazole) Fe(II), [Fe[$(C_{16}H_{16}N_{16})Cl_2$] (3a)

0.05 mol of (4-Cyano-5-aminopyrazole) was added slowly to an anhydrous iron (II) chloride solution (0.01 mol) under similar reaction conditions as described above. The resulting mixture was stirred for about 3 hrs. leading to the formation of pale yellow amorphous solid which was filtered, thoroughly washed with EtOH followed by Et_2O and vacuum dried [Yeild 70%, M.Pt. 342°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Co(II),

$[Co[(C_{16}H_{16}N_{16})Cl_2]$ (4a)

Anhydrous cobalt (II) chloride solution in THF (0.01 mol) was dropwise added to 0.05 mol of ligand solution at room temperature. The resulting solution was stirred on a magnetic stirrer for 3 hrs. under dry N_2 atmosphere. An amorphous, dark brown solid product was obtained, which was filtered, washed with THF and Et_2O and dried in vacuum [Yeild 65%, M.Pt. 350°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Ni(II)

$Ni[(C_{16}H_{16}N_{16})Cl_2]$ (5a)

The compound $Ni[(C_{16}H_{16}N_{16})Cl_2]$ was prepared by adding the ligand solution (0.05 mol) to anhydrous nickel (II) chloride (0.01 mol) at room temperature followed by magnetic stirring. This has resulted in the formation of green needle shape crystalline product which was isolated in the manner described above [Yeild 69%, M.Pt. 333°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Cu(II)

$[Cu[(C_{16}H_{16}N_{16})Cl_2]$ (6a)

A hot solution of ligand (0.05 mol) in EtOH (30 cm^3) was mixed with anhydrous copper (II) chloride solution (0.01 mol) in THF and the reaction mixture was stirred for about 4 hrs. under dry N_2 atmosphere in THF and the reaction mixture was

stirred for about 4 hrs. yeilding green colored crystalline product which was isolated by filteration, followed by washing with Et.OH and Et_2O and Vacuum dried. [Yeild 71%, M.Pt. 360°C].

Reaction of $H4CN5NH_2pz$ with $[M(PPh_3)_2Cl_2]$, Synthesis of Dichlorotetrakis (4-Cyano-5-aminopyrazole) Metal(II) complexes ML_4Cl_2 [M = Mn(II), Co(II), Ni(II)].

The following preparative procedures have been adopted.

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Mn(II) $[Mn(C_{16}H_{16}N_{16})Cl_2]$. (2a')

The precursor $[Mn(PPh_3)_2Cl_2]$ (0.01 mol) disssolved in 80 cm^3 of THF was slowly reacted with (0.05 mol) of ligand solution taken in 40 cm^3 EtOH, in a closed reaction vessel under dry N_2 atmosphere at room temperature. The reaction mixture was constantly stirred for 1 hr. resulting in the isolation of solid mass. The solid thus obtained was filtered and washed several times with ether and dried in vacuo. The ether washing on drying in vacuo gave a colour less microcrystalline solid mass equivalent to 2 mol. identified as Ph_3P on the basis of microanalysis, melting points and i.r. spectral studies [Yeild, 60%, M.Pt. 353°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Co(II), $[Co(C_{16}H_{16}N_{16})Cl_2]$. (4a')

The compound $[Co(C_{16}H_{16}N_{16})Cl_2]$ was prepared by adding

the ligand soution (0.05 mol) in THF to (0.01 mol) $[Co(PPh_3)_2Cl_2]$ solution in THF under similar reaction conditions described above. The reaction mixture was magnetically stirred for 1 hr. leading to the formaion of a crystalline brown product obtained, which was filtered, washed several times with ether and vacuum dried. The mother liquor on evaporation under vacuum left 2 mol equivalent of PPh_3 identified on the bais of microanalysis and i.r. spectral studies [Yeild 70%, M.Pt. 345°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Ni (II)

$[Ni(C_{16}H_{16}N_{16})Cl_2]$ (5a')

0.01 mol of $[Ni(PPh_3)_2Cl_2]$ dissolved in 80 cm^3 of THF was gradually added to an excess of ligand solution (0.050 mol) in EtOH at room temperature under dry N_2 atmosphere resulting in the isolation of crystalline solid product. The product thus formed was filtered, washed with ether and dried in vacuum. The mother liquor collected on filteration and washing left 2 mol equivalent of the colourless microcrystalline solid, identified as PPh_3. [Yeild 69%, M.Pt. 337°C].

Reaction of $H4CN5NH_2pz$ with anhydrous group II B Metal chlorides, MCl_2, Synthesis of Dichlorotetrakis (4-Cyano-5-aminopyrazole) Metal (II) complexes, ML_4Cl_2 [M = Zn, Cd, Hg].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Zn(II)

$Zn[(C_{16}H_{16}N_{16})Cl_2]$ (7a)

0.01 mol of Zinc(II) chloride solution in 50cm^3 THF was slowly reacted with 0.045 mol of the ligand solution in EtOH. The reaction mixture was continuously stirred for 3 hrs at room temperature under dry N_2 atmosphere resulting in the isolation of colourless solid mass which was isolated in a manner described above [Yeild 67%, M.Pt. 336°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Cd(II)

$Cd[(C_{16}H_{16}N_{16})Cl_2]$ (8a).

The preparation of the above complex was accomplished by reacting 0.01 mol of $CdCl_2$ dissolved in THF with slightly more than the stoichiometric amount of ligand (o.045 mol) in EtOH at room temperature. The reaction mixture was stirred for 3 hrs under dry N_2 atmosphere resulting in the formation of colourless solid mass which was filtered, washed thoroughly with THF and Et_2O and dried in vacuum [Yeild 65%, M.Pt. 355°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Hg(II)

$Hg[(C_{16}H_{16}N_{16})Cl_2]$ (9a)

A solution of the ligand (0.045 mol) in 30 cm^3 of EtOH was slowly added to a suspension of the anhydrous $HgCl_2$ (0.01 mol) in 50 cm^3 of THF at room temperature. The reaction mixture was stirred for 3 hrs in a closed reaction vessel under dry N_2 atmosphere when a solid seperated. It was

filtered, washed several times with ethanol followed by ether and dried in vacuum [Yeild 62%, M.Pt. 362°C].

Reaction of H4CN5NH$_2$pz with triphenyl phosphine derivatives of group IIB metals, [M((PPh$_3$)$_2$Cl$_2$]; Synthesis of dichloro-tetrakis (4-Cyano-5-aminopyrazole), Metal (II) chlorides, ML$_4$Cl$_2$ [M=Zn, Cd, Hg].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Zn (II) [Zn[(C$_{16}$H$_{16}$N$_{16}$)Cl$_2$] (7a').

The 0.01 mol of [Zn(PPh$_3$)$_2$Cl$_2$] dissolved in THF (80 cm^3) was reacted with 0.05 mol of ligand solution in EtOH. The reaction contents were stirred for 1 hr under dry N_2 atmosphere at room temperature, resulting in the formation of colourless amorphous solid. The solid product thus obtained was filtered off, washed several times with ether and dried in vacuo. The mother liquor on evaporation gave colourless microcystalline substance which was identified as PPh$_3$ on the basis of m.p and i.r. spectral studies. [Yeild 68%, M.Pt. 320°C].

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Cd(II) [Cd(C$_{16}$H$_{16}$N$_{16}$)Cl$_2$] (8a')

0.05 mol solution of ligand in Et.OH(40 cm^3) was reacted with precursor complexes [Cd(PPh$_3$)$_2$Cl$_2$] (0.01 mol) dissolved in 80 cm^3 of THF in a closed reaction vessel under dry N_2 atmosphere at room temperature. The reaction mixture was

constantly stirred for 1 hr. when a solid mass was obtained. It was filtered, washed several times with ether and dried in vacuum. The ether washings on drying in vacuo gave a colourless microcrystalline solid mass identified as PPh_3 on the basis of microanalysis, M.Pt. and i.r. spectral studies. [Yeild 72%, M.Pt. 327°C]

Dichlorotetrakis (4-Cyano-5-aminopyrazole) Hg(II) $[Hg(C_{16}H_{16}N_{16})Cl_2]$. (9a')

The complex $[Hg(C_{16}H_{16}N_{16})Cl_2]$ was prepared by stirring $Hg(PPh_3)_2Cl_2$ (0.01 mol) and the ligand solution (0.045 mol) at room temperature about 3 hrs. under dry N_2 atmosphre. The colourless solid thus obtained was filtered, washed and dried in vacuo [Yeild 65%, M.Pt. 358°C].

Analysis and Physical Measurements

The elemental analysis for C, H, N was carried out in micro-analytical laboratory of the Indian Institute of Technology, Delhi. Metals were estimated by complexometric-titration[23] with standard EDTA solution and the estimation of chlorine was done gravemetrically[24]. The infrared spectra (4000-200 cm^{-1}) were recorded as KBr discs on a Perkin-Elmer 621 Spectrophotometer. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C.

Diffuse relectance spectra were recorded on a Carl-Zeiss VSU-2P spectrophotometer using MgO as calibrant. Electrial conductivity values were measured on Systronic 302 conductivity bridge. Electronic spectra in DMSO were recorded on a Pye Unicam 8800 spectrophotometer at room temperature. Molecular weights of the compounds were determined using camphor as solvent by the Rast method[25].

RESULTS AND DISCUSSION

The results of elemental analyses (Table 1) are consistent with the proposed stoichiometry as $[ML_4Cl_2]$; [M=Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg] with L = $4CN5NH_2pz$ suggesting the following mode of reaction.

$$MCl_2 + 4L \longrightarrow ML_4Cl_2$$

[L=$H4CN5NH_2pz$, M=Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II)].

However, the reactions with precursors $[M(PPh_3)_2Cl_2]$ under similar condition liberate two mole equivalent of PPh_3 yeilding the complexes having composition $ML_4\ Cl_2$ [M =Mn, Co, Ni, Zn, Cd, Hg] proposed on the basis fo results of elemental analysis (Table-1) as shown below :

$$[M(PPh_3)_2Cl_2] + 4L \longrightarrow ML_4Cl_2$$

TABLE-1: Elemental Analysis, Molecular Weights and Molar Conductivity Values of the Compounds.

Compounds	Found (Calcd.) %					Molecular Weight[a] Found (Calcd.)	Molar conductivity[b] $cm^2 ohm^{-1} mole^{-1}$
	M	Cl	C	N	H		
$CrC_{16}H_{16}N_{16}Cl_2$	9.31 (9.36)	12.68 (12.77)	34.71 (34.60)	40.43 (40.37)	2.69 (2.88)	549±1 (555.2)	21.4
$MnC_{16}H_{16}N_{16}Cl_2$	9.77 (9.84)	12.62 (12.70)	34.32 (34.42)	40.01 (40.15)	2.73 (2.86)	561±1 (558.1)	26.3
$MnC_{16}H_{16}N_{16}Cl_2$	9.81 (9.84)	12.69 (12.70)	34.51 (34.42)	40.28 (40.15)	2.69 (2.86)	556±1 (558.1)	23.8
$FeC_{16}H_{16}N_{16}Cl_2$	9.79 (9.99)	12.54 (12.68)	34.36 (34.38)	39.97 (40.07)	2.81 (2.86)	550±1 (558.9)	25.2
$CoC_{16}H_{16}N_{16}Cl_2$	10.36 (10.48)	12.58 (12.62)	34.11 (34.19)	39.87 (39.86)	2.80 (2.85)	545±1 (562.0)	29.3
$CoC_{16}H_{16}N_{16}Cl_2$	10.42 (10.48)	12.55 (12.62)	34.12 (34.19)	39.84 (39.86)	2.82 (2.85)	540±1 (562.0)	22.6
$NiC_{16}H_{16}N_{16}Cl_2$	10.39 (10.45)	12.61 (12.62)	34.12 (34.87)	39.81 (39.87)	2.81 (2.85)	560±1 (562.8)	18.8
$NiC_{16}H_{16}N_{16}Cl_2$	10.44 (10.45)	12.61 (12.62)	34.11 (34.21)	39.77 (39.87)	2.82 (2.85)	570±1 (562.8)	25.9
$CuC_{16}H_{16}N_{16}Cl_2$	11.12 (11.21)	12.45 (12.51)	33.89 (33.91)	39.43 (39.53)	2.71 (2.82)	570±1 (566.6)	24.6
$ZnC_{16}H_{16}N_{16}Cl_2$	11.56 (11.49)	12.54 (12.47)	33.62 (33.79)	39.30 (39.42)	2.71 (2.81)	573±1 (568.6)	19.4
$ZnC_{16}H_{16}N_{16}Cl_2$	11.33 (11.49)	12.60 (12.47)	33.61 (33.79)	39.54 (39.42)	2.62 (2.81)	570±1 (568.6)	20.5
$CdC_{16}H_{16}N_{16}Cl_2$	18.05 (18.25)	11.39 (11.51)	31.02 (31.21)	36.38 (36.41)	2.49 (2.59)	6.09±1 (616.0)	25.3
$CdC_{16}H_{16}N_{16}Cl_2$	18.12 (18.25)	11.43 (11.51)	31.12 (31.21)	36.29 (36.41)	2.51 (2.59)	603±1 (616.0)	22.4
$HgC_{16}H_{16}N_{16}Cl_2$	28.22 (28.50)	10.03 (10.07)	27.13 (27.30)	31.68 (31.84)	2.33 (2.27)	708±1 (704.0)	23.6
$HgC_{16}H_{16}N_{16}Cl_2$	28.31 (28.50)	10.16 (10.07)	27.09 (27.30)	31.66 (31.84)	2.13 (2.27)	689±1 (704.0)	23.3

Obtained after following the reaction by equation (1) and (2).

a- In Camphor

b- In DMSO at the 1 mM level

[L=H4CN5NH$_2$pz, M=Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II)].

All the complexes either obtained from anhydrous metal chlorides or their triphenylphosphine derivatives have been found to be soluble in most non-polar solvent and the observed molecular weight (Table-1) suggest their monomeric nature. However, the observed low values of molar conductance in DMSO (Table -1) indicate that they are non-electrolytes.

The I.R. spectrum of pyrazole with complete assignments is well documented in literature[26,27] for the several states of the ligand. The IR spectrum of the ligand H4CN5NH$_2$pz (Table 2) exhibits bands comparable to those reported[26,27] for pyrazole ligand. The N-H stretching vibration appear at considerably lower wave number attributable to intra or intermolecular hydrogen bonding[3, 4]. However, the N-H bending vibration reported[28] for the solid pyrazole has not been observed in the present ligand. The vibrations associated to the pyrazole ring such as ring vibrations (R_1, R_2, R_3 and R_4) appear at their estimated positions. The C-H stretching and C-H bending vibrations too, appear at the expected positions. The band appearing at 1490 cm^{-1} as a medium intensity band may, presumably, be assigned for C=N stretching vibration consistent with the free benzopyrazoles[29]. A very strong band at 2250 cm^{-1} may reasonably, be assigned for C≡N stretching vibration similar to that reported[30-32] for the free -C≡N

TABLE-2: Infra-red Vibrational Frequencies (cm-1) of the Ligand and the Complexes.

Comocunds	ν N-H Str.	NH_2 group Vibrations.	ν C-H Str. ν C-H Bend.	Ring Vibrations	ν C ≡ N	ν M-N	ν M-Cl
Ligand	2920sb	3400s 3350s 3300s 1610vs	3150s 1065s 1040s 870m	1490s 1390m 1340s 940m	2250		
1a	3440s	3415s 3350s 3310sh 1610vs	3155s 1055s 1035m 875msh	1480s 1395m 1345s 955w	2255vs	225s	285m
2a	3435s	3410s 3355s 3305s 1610vs	3150s 1060s 1035s 890m	1475s 1395s 1345s 955w	2250vs	230s	280m
2a′	3435s	3400s 3350s 3310m 1610vs	3160s 1065s 1040msh 885w	1485s 1390m 1350s 990w	2255vs	230s	285m
3a	3425s	3410s 3355s 3315m 1610vs	3155m 3130sh 1055s 1030m 880m	1475s 1390m 1350sh 950m	2250vs	235s	285m
4a	3435s	3405s 3350s 3300s 1615vs	3160m 3130sh 1060s 1035m	1480m 1395m 1350s 940w	2250vs	230s	280m
4a′	3420s	3410s 3360m 3310sh 1610vs	3150s 1060s 1035s 875m	1475s 1395m 1355s 950m	2250vs	230s	290m
5a	3430s	3410s 3350m 3320m 1605vs	3155s 1065s 1040s 880m	1485s 1390m 1345w 950m	2250vs	220s	285m
5a′	3420s	3400s 3350m 3310s 1610vs	3150s 1065m 1035s 875m	1480s 1390m 1345sh 945m	2250vs	230s	280m

Contd.

Compounds	ν_{N-H} Str.	NH_2 group Vibrations.	ν C-H Str. ν C-H Bend.	Ring Vibrations	ν C ≡ N	ν M-N	ν M-Cl
6a	3435s	3410s 3350m	3155s 1070s	1475s 1390m	2250vs	235s	280m
7a	3430s	3410s 3350s 3310m 1610vs	3155s 1065s 1040s 875m	1485s 1395s 1340s 935m	2250vs	235s	290m
7a′	3440s	3410s 3350s 3310m 1610vs	3155s 1060s 1035m 860sn	1480s 1395m 1345s 950msn	2250vs	235s	290m
8a	3435s	3415s 3345s 3305ssn 1615vs	3150s 1065s 1045s 880m	1485s 1390m 1345s 950m	2250vs	230s	285m
8a	3430s	3415s 3340s 3200s 1610vs	3150s 1060s 1040m 870m	1480s 1390m 1345s 955w	2255vs	235s	275m
9a	3435s	3420s 3350s 3305msn 1615vs	3155s 1060s 1050m 890w	1475s 1395m 1340s 950m	2250vs	220s	285m
9a′	3440s	3415s 3445s 3300m 1610vs	3150s 1060s 1055sn 885m	1480s 1390ssh 1350s 960msn	2250vs	225s	285m

vs= very strong, s= strong, ssh= strong shoulder, msn= medium shoulder, m= medium, w= weak.

group. However, a multiplet (three medium to strong intensity bands) in the region 3300-3400 cm^{-1} alongwith a strong band at 1610 cm^{-1} may be assigned for NH_2 group vibrations.

The bands observed in the i.r. spectra of the complexes derived either from anhydrous metal chlorides or their triphenylphosphine derivatives (Table 2) were compared with the free ligand vibrations. The bands corresponding to --C≡N and-NH_2 groups appear at the same frequency regions as recorded for free ligand, ruling out possibility of their coordination to the metal ions. However, there is a considerable positive shift in the N-H stretching vibration attributable to differences in the internal or external hydrogen bonding[3,4] indicating the coordination of the ligand via pyridyl nitrogen N(2). The coordination via pyridyl nitrogen N(2) has been further corroborated by a slight negative shift (5-15cm^{-1}) in the C≡N stretching vibration as reported for benzopyrazole complexes[29].

A strong band in the frequency region 220-235 cm^{-1} may, reasonably be assigned as M-N stretching vibration consistent with that expected for octahedral complexes derived from nitrogen donor ligands[33-35]. However, a medium band in the frequency region 280-290 cm^{-1} is assigned as M-Cl stretching vibration. The complexes derived from triphenyl phosphine derivatives of metal chlorides, $[M(PPh_3)_2Cl_2]$ do not show band characterisitc of Ph_3P moiety reported[36] to appear ca 500 cm^{-1}

suggesting a complete loss of PPh_3 group during the reaction.

Further information regarding the mode of coordination of the ligand to metal ions and the stereochemistry around the metal ions has been obtained by magnetic susceptibility measurements and ligand field studies as discussed below :

The reflectance spectra and electronic spectra of ML_4Cl_2 in non-polar solvents are quite comparable suggesting the similar species in the solid as well as in solution.

The observed magnetic moment (μeff) for Cr(II) complexes (1a) and a weak band in its reflectance and electronic spectra at ca 15,000 cm^{-1} assigned to $^5E_g \longrightarrow {}^5T_{2g}$ transition (Table 3) are consistent with the octahedral geometry around Cr(II) ion[3,4,37]. However, the ligand field spectra of (2a) and (2a') exhibit two bands assignable to $^4T_{2g}(G) \longleftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \longleftarrow {}^6A_{1g}$ transitions, respectively (Table 3). The observed values of magnetic moments further corroborate the ground state as $^6A_{1g}$ confirming the octahedral geometry of these compounds.

The μeff value for Fe(II) complex (3a) and a weak band in the ligand field spectrum at Ca 12,100 which assignable to the transition $^5E_g \longleftarrow {}^5T_{2g}$ (Table 3), consistent with an octahedral environment around the metal ions[3,4, 36]. However, a shoulder reported[3,4,36] to appear at Ca, 10,000 in other pyrazole complexes was not observed.

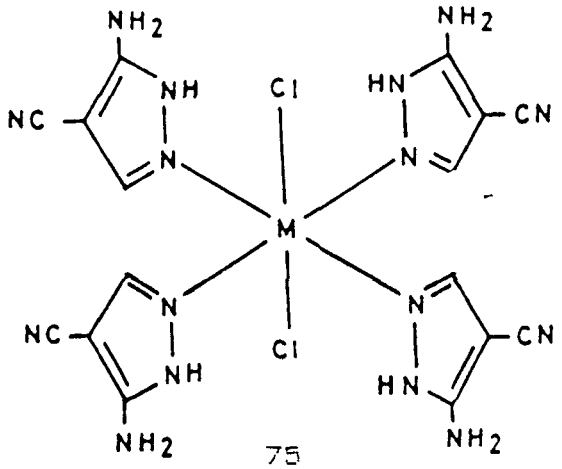
TABLE-3: μ_{eff}(B_1M.) ligand Field Bands Observed in the Reflectance and Electronic Spectra in cm^{-1} and their Assignments.

Complexes	μ_{eff}	Bands Positions[a]	Assignments
1a	4.79	14,975 (14,700)	$^5T_{2g} \leftarrow {}^5E_g$
2a	5.83	22,472 (22,345) 18,763 (18,519)	$^4T_{2g}(G) \leftarrow {}^6A_{1g}$ $^4T_{2g}(G) \leftarrow {}^6A_{1g}$
2a'	5.88	22,222 (22,130) 18,519 (18,182)	$^4T_{2g}(G) \leftarrow {}^6A_{1g}$ $^4T_{1g}(G) \leftarrow {}^6A_{1g}$
3a	5.45	12,100 (11,950)	$^5E_g \leftarrow {}^5T_{2g}$
4a	4.49	20,667 (20,619) 19,608sh (19,380sh)	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ $^4A_{1g}(F) \leftarrow {}^4T_{1g}(F)$
4a'	4.55	20,747 (20,408) 19,418sh (19,230sh)	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ $^4A_{1g}(P) \leftarrow {}^4T_{1g}(F)$
5a	2.83	27,500 (27,450) 18,100 (17,980)	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$
5a	2.91	27,777 (27,667) 17,900 (17,690)	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ $^3T_{1g}(F) \leftarrow {}^3A_{2g}$
6a	1.85	16,767 (16,600)	$^2T_{2g} \leftarrow {}^2E_g$

[a]Position in $CHCl_3$ solution given in parentheses.

The observed values of magnetic moments for the complexes (4a), (4a'), (5a),(5a') are slightly higher than that of calculated spin-only values. This may be understood in terms of spin-orbit coupling contributios. However, these values lie in the range normally observed for various spin-free Co^{2+}, and Ni^{2+} octahedral complexes of pyrazoles. The ligand field spectra of (4a) and (4a') exhibit a main band maxima centered at Ca 19,500 cm^{-1} which may be reasonably be assigned to $^4A_{2g}$ (F) $\longleftarrow$ $^4T_{1g}$ (F) and $^4T_{1g}$(P) $\longleftarrow$ $^4T_{1g}$ (F) transitions, respectively confirming an octahedral environment around Co^{2+} ion. However, two strong ligand field bands recorded at Ca 27,700 cm^{-1} and 17,600 cm^{-1} for (5a) and (5a') complexes corresponds to $^3T_{1g}$ (P) $\longleftarrow$ $^3A_{2g}$(F) and $^3T_{1g}$(F) transition respectively similar to that reported for octahedral complexes of Ni^{2+} ion.

The observed magnetic moment and a broad weak band in the electronic spectra of (6a) suggest an octahedral geometry (Table 3). The physico-chemical data described in the above paragraphs help to visualize the structure of these complexes as shown below.



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CHAPTER - IV

SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF COMPLEXES OF 4-CYANO-5-AMINOPYRAZOLIDE ION $[4CN5NH_2PZ]^-$ AND 3,4-DICYANO-5-AMINOPYRAZOLIDE ION $[3,4(CN)_25NH_2PZ]^-$ WITH COBALT, COPPER AND SILVER.

INTRODUCTION

A variety of pyrazolide ion complexes have been reported[1-5] in basic medium where the pyrazole molecule loses the proton from N(1) to form the uninegative, potentially exobidentate pyrazolide ion, which can bridge between two similar or dissimilar metals. The polymerization in the formation of these complexes can be avoided by the use of appropriate capping groups on the metals, allowing the isolation of dimeric species.[6].

Polymeric complexes of the type $[M(pz)_m]_n$ [M=Ag for m=1, and Fe and Cu for m=2] have been reported[7] to be formed in basic medium containing the exobidentate 1,2-dihaptopyrazolide moiety.

Pyrazolides of many divalent transition metal have been prepared by the reaction of ammonical solution of the metal salts with pyrazole. The polymeric chelates are solvated with water and/or ammonia but may be obtained pure by drying in vacuo. The polymeric pyrazolides are intractable, thermally very stable solids. The $[Cu(pz)_2]_n$ polymer may be obtained as a brown solid when reaction was performed in ammonia. The brown modification can be converted to green one upon heating with excess of pyrazole[8]. Among the various transition metal pyrazolides the most, thoroughly studied one is the insoluble purple cobalt chelate, $[3,5\text{-}Me_2(Pz)_2Co]_n$ which can be precipitated in analytical purity at pH 7.5-9.0.

Dimeric complexes of titanium $[TiCp_2(pz)]_2$ has been produced[9] which has allowed a new mode of pyrazolate bonding. In order to explain the role of steric factors in the formation of monomeric compounds and to learn more about the pyrazolate ion as a ligand. Eigenbrot and Raymond have adjusted the size and number of cyclopentadienide ligands anticipitating that a reduction in the total steric bulk of the other ligands might lead to the formation of one or more dimeric species involving compound $UCp^*_2Cl_2$ ($Cp^* = C_5Me_5$) as the starting material[10,11]. The X-ray structures of the compounds $U(C_5Me_5)_2\,Cl(pz^-)$ and $U(C_5Me_5)_2(pz^-)$ derived by the reaction of $UCp^*_2Cl_2$ with the stoichiometric amount of $Na(pz)^-$ have been proved to be the monomers rather than the dimers[12].

Pyrazolate-bridged binuclear palladium (II) complexes of the type $[Pd_2X_2(\mu\text{-}L\text{-}L)_2(PR_3)_2]$ [L-L = pz (pyrazolate) or dmpz (3,5-dimethylpyrazolate); X =Cl, Br or I; PR_3 = PBu_3, PMe_2Ph or $PMePh_2$] have been prepared[13]. They were characterized by elemental analysis. ^1H and ^{31}PNMR spectra data and in the case of $[Pd_2Cl_2(\mu\text{-dmpz})_2\,(PMe_2Ph)_2]$ by single crystal X-ray diffraction methods. The structure determination shows two Pd atoms bridged by two $[dmpz]^-$ ligands which form asymmetric Pd-N bond distances, an observation that may be correlated with the different trans influences associated with the Cl and P atoms which complete the square-planar geometries about the Pd.

This chapter deals with the preparation of complexes of the 4-cyano-5-aminopyrazolide ion, $[4CN5NH_2pz]^-$ and 3,4-dicyano-5-aminopyrazolide ion $[3,4\ (CN)_25NH_2pz]^-$ with Cobalt(I), Copper (I) and Silver (I) and their triphenylphosphine derivatives.

EXPERIMENTAL

Starting Materials

The ligands 4-cyano-5-aminopyrazole and 3,4-dicyano-5-aminopyrazole were prepared by the reported methods[14,15]. The purity of the ligands was checked by microanalysis i.e. i.r. m.pt. and molecular weights. The triphenylphosphine derivatives of Co(I), Cu(I) and Ag(I) were prepared by reported methods[16-19]. Copper (I) chloride was prepare by a literature procedure[20]. AgCl(Fluka) was used as such. All solvent were purifed and dried before use.

Preparation of Chlorotris (triphenyl phosphine) Cobalt (I) $Co(PPh_3)_3Cl$

15 m mol (3.93 gm) triphenyl phosphine was dissolved in 100 cm^3 $CHCl_3$ in which 5 m mol (0.65 gm) $CoCl_2$ was added in portions with continuous stirring and then dry 100 Cm^3 ethanol was added followed by vigorous stirring for 2 hours. A stable green, crystalline solid separated out (m.pt. 176°C).

Preparation of Chlorotris (triphenyl phosphine) Copper (I) $Cu(PPh_3)_3Cl$

Triphenylphosphine (6.55gm, 25m mol) was dissolved in 100 cm^3 of $CHCl_3$ in which Cu(I) Chloride (0.6015 gm, 6.5 m mol) was added in portions with continuous stirring, 400 cm^3 of dry ethanol was added followed by vigorous stirring for 2 hrs. A shining white microcrystalline solid separated out [m.pt. 150-160°].

Preparation of Chlorotris (triphenyl phosphine) Silver (I) $[Ag(PPh_3)_3NO_3]$

Silver nitrate (5.02 gm, 29.6 m mol) dissolved in a mixture of acetonitrile and 20 cm^3 of methanol was added at once to triphenylphospine (17.78 gm, 66.1 m mol) in 50 cm^3 of methanol, crystals of $[Ag(PPh_3)_3NO_3]$ began to form within few minutes and were collected after standing overnight at room temperature.

Reaction of $H4CN5NH_2pz$ or H 3,4 $(CN)_25NH_2pz$ with Metal (I) Chlorides; Synthesis of 1,2-diphapto 4-cyano-5-amino pyrazolido or 3, 4 dicyano-5- aminopyrazolido metal (I) oligomer $[M(4CN5NH_2pz)]_n$ or $[M(3,4(CN)_25NH_2pz]_n$ [M=Cu(I), Ag(I)].

Reaction of $H4CN5NH_2pz$ or H3, $4(CN)_25NH_2pz$ with Copper (I) Chloride; Synthesis of 1,2-dihapto 4-cyano-5-aminopyrazolido or 3,4-dicyano-5-aminopyrazolido Copper (I), oligomer. $[Cu(4CN5NH_2pz)]_n$ or $[Cu(3,4(CN)_25NH_2pz)]_n$.

A 0.02 mol ammoniacal solution of CuCl (50 cm^3) has been reacted with 0.025 mol solution of $H4CN5NH_2pz$ or $H3,4(CN)_25NH_2pz$. taken in 40 cm^3 of ethanol. The reaction mixture was stirred mechanically for 3 hours resulting in the formation of colorless sticky products. These compounds were washed several times with ethanol followed by diethyl ether and dried in vacuo. The compounds were insoluble in almost all the polar and non-polar solvents. Yeilds 72% and 69%; Decomposition temp., 250°C and 260°C for $[Cu(4CN5NH_2pz)]_n$ and $[Cu(3,4(CN)_25NH_2pz)]_n$, respectively.

Reaction of $H4CN5NH_2pz$ or H3, $4(CN)_25NH_2pz$ with Silver(I) Chlorides; Synthesis of 1,2-dihapto-4-cyano-5-aminopyrazolido or 3,4-dicyano-5-aminopyrazolido silver (I) oligomer. $[Ag(4CN5NH_2pz)]_n$ or $[Ag(3,4(CN)_25NH_2pz)]_n$

An excess of $H4CN5NH_2pz$ or H3, $4(CN)_25NH_2pz$ (0.025 mol) solution in 40 cm^3 ethanol was added to an ammoniacal solution of silver (I) chloride, resulting in the immediate seperation of colorless solid mass. The mixture was stirred for 3 hours resulting in the formation of solid products which were filtered washed several times with ether and dried in vacuo. Yeilds 71% and 68%; Decomposition temp., 270°C and 290°C for $[Ag(4CN5NH_2pz)]_n$ and $[Ag(3,4(CN)_25NH_2pz)]_n$, respectively.

Reaction of $H4CN5NH_2pz$ or H3, $4(CN)_25NH_2pz$ with $(PPh_3)_3CoCl$; Synthesis of Bis (1,2-dihapto-4-cyano-5-aminopyrazolido)bis (triphenylphosphine) Co(I) or Bis (1,2-dihapto-3,4-dicyano-5-aminopyrazolido)bis(triphenylphosphine) Co(I), $[Co(PPh_3)_2(4CN5NH_2)pz]_2$ or $[Co(PPh_3)_2\ (3,4(CN)_25NH_2pz)]_2$.

An excess of ligand (0.020 mol) in ethanol (50 cm^3) was slowly added to ammoniacal solution of $Co(PPh_3)_3Cl$. The resulting reaction mixture was mechanically stirred for 3 hrs. The resulting solid mass thus obtained was filtered, washed several times with ethanol followed by diethyl ether and dried in vacuo. The mother liquor obtained after filteration and washing left colourless microcrystalline solid mass on evaporation which identified as PPh_3 on the basis of micro-analysis, m.pt. and i.r. spectral studies Yeilds 73% and 68%; M.Pt. 267°C and 278°C for $[Co(PPh_3)_24CN5NH_2pz]_2$ and $[Co(PPh_3)_2\ 3,4(CN)_25NH_2pz]_2$, respectively.

Reaction of $H4CN5NH_2pz$ or H3,4 $(CN)_25NH_2pz$ with $(PPh_3)_3CuCl$; Synthesis of Bis(1,2-dihapto-4-cyano-5-aminopyrazolido)bis (triphenylphosphine) Cu(I) or Bis (1, 2-dihapto-3, 4-dicyano-5-aminopyrazolido) bis(triphenylphosphine) Cu(I), $[Cu(PPh_3)_2(4CN5NH_2pz)]_2$ or $[Cu(PPh_3)_2(3,4(CN)_25NH_2pz)]_2$.

A 0.020 mol solution of ligands in ethanol (50 cm^3) was slowly added to 0.020 mol ammoniacal solution of $[Cu(PPh_3)_3Cl]$ resulting in the formation of solid products at room

temperature. The product thus formed was filtered, washed several times with ethanol and then with ether and dried in vacuum. The mother liquor alongwith the ethanol and ether washing left colorless microcrystalline solid identified as PPh_3 on the basis of microanalysis, m.pt. and i.r. spectral studies. Yeilds 73% and 65%; M.Pt. 237°C and 245°C for $[Cu(PPh_3)_2 4CN5NH_2pz]_2$ and $[Cu(PPh_3)_2 3,4(CN)_2 5NH_2pz]_2$, respectively.

Reaction of $H4CN5NH_2pz$ or $H3,4(CN)_2 5NH_2pz$ with $(PPh_3)_3AgNO_3$; Synthesis of Bis (1,2-dihapto-4-cyano-5-aminopyrazolido) bis (triphenylphosphine)Ag(I) or Bis (1,2-dihapto-3,4-dicyano-5-aminopyrazolido) bis(triphenylphosphine) $[Ag(PPh_3)_2-(4CN5NH_2pz)]_2$ or $[Ag(PPh_3)_2(3,4(CN)_2\ 5NH_2pz)]_2$.

An excess of ligand in ethanol ($50Cm^3$) was slowly added to 0.20 mol of an ammonical solution of $Ag(PPh_3)_3NO_3$, resulting in the formation of yellowish white solid product. It was filtered off, washed several times with ethanol followed by diethylether and dried in vacuo. The mother liquor, alongwith the washing of ethanol and diethylether, was evaporated to leave a colourless microcrystalline solid identified as triphenylphosphine on the basis of microanalysis m.pt. and i.r. spectral studies. Yeilds 70% and 73%; M.Pt. 254°C and 262°C for $[Ag(PPh_3)_2 4CN5NH_2pz]_2$ and $[Ag(PPh_3)_2 3,4(CN)_2 5NH_2pz]_2$, respectively.

Chemical analysis

Elemental analysis were carried out in the Micro-analytical laboratory of the IIT, Delhi. The metals,cobalt, copper and silver were estimated by reported[20,21] methods. I.r. , spectra (4000-200 cm^{-1}) were recorded as KBr discs on a Perkin Elmer 621 Spectrophotometer. Magnetic susceptibility measure-ments were carried out using a Faraday balance at 25°C. Molecular weights were determined by Rast methods[22].

RESULTS AND DISCUSSION

The reaction of ammoniacal solutions of MCl [M = Cu(I), Ag(I)] with H4CN5NH_2pz or H3,4$(CN)_2$5NH_2pz resulted in the formation of colorless sticky solid compounds. The analytical data (Table 1) suggest that the complexes are formed in 1:1 stoichiometry. These compounds have been found to be highly insoluble in almost all the polar and non-polar solvents indicating their polymeric nature analogous to that reported[23,24] for $[Cupz]_n$ and $[Agpz]_n$.

However, the reaction of ammoniacal solution of triphenylphosphine derivatives of Co(I), Cu(I) and Ag(I), $[M(PPh_3)_3X]$ M = Co and Cu for X = Cl or Ag for X = NO_3 with H4CN5NH_2pz or H3, 4-$(CN)_2$5NH_2pz result in the formation of solid products of the type $[M(PPh_3)_2(4CN5NH_2pz]_2$ or $[M(PPh_3)_2$ 3,4$(CN)_2$5NH_2pz$]_2$. Ph_3P equivalent to 1 mol is liberated (see experimental section). The compounds are soluble in most of organic solvents. The analytical data (Table 1) suggest that these complex too have 1 : 1 stoichiometry. The experimentally determined molecular weight data suggest their dimeric nature, whilst the low electrical conductivities (Table 1) confirm their non-ionic nature.

The nature of bonding of the ligands in the compounds derived either from metal (I) chlorides or triphenylphosphine derivatives of metal (I) chlorides has been inferred by comparative study of the i.r. spectra of the free ligands and

Table-1 : Elemental Analyses and Molecular Weights.

Compound	Colour	Found (Calcd.) %				Molecular weight Found (Calcd.)
		M	C	N	H	
$[Cu(4CN5NH_2oz)]_n$	white	37.2 (37.1)	28.1 (28.2)	2.8 (32.6)	1.7 (1.9)	- -
$[Cu(3,4(CN)_25NH_2oz)]_n$	white	32.4 (32.9)	30.05 (30.69)	35.15 (35.88)	1.0 (1.02)	- -
$[Ag(4CN5NH_2oz)]_n$	white	50.1 (50.2)	22.3 (22.4)	26.0 (26.1)	1.3 (1.4)	- -
$[Ag(3,4(CN)_25NH_2oz)]_n$	white	44.85 (44.95)	24.5 (25.02)	29.31 (29.19)	0.83 (0.83)	-
$[Co(PPh_3)_2(4CN5NH_2oz)]_2$	Light blue	10.45 (10.40)	72.60 (72.45)	8.4 (8.2)	4.8 (4.6)	1379.04 (1379.00)
$[Co(PPh_3)_2(3,4(CN)_25NH_2oz)]_2$	Light blue	8.15 (8.25)	68.0 (68.8)	9.9 (9.79)	4.31 (4.47)	1429.1 (1430.0)
$[Cu(PPh_3)_2(4CN5NH_2oz)]_2$	Yellowish white	9.1 (9.1)	69.1 (69.2)	8.0 (8.1)	4.7 (4.9)	1390.0 (1390.4)
$[Cu(PPh_3)_2(3,4(CN)_25NH_2oz)]_2$	Yellowish white	8.72 (8.82)	65.8 (65.8)	9.62 (9.72)	4.31 (4.41)	1438.1 (1439.0)
$[Ag(PPh_3)_2(4CN5NH_2oz)]_2$	Yellowish white	14.5 (14.6)	64.9 (64.9)	7.6 (7.6)	4.4 (4.6)	1478.0 (1478.0)
$[Ag(PPh_3)_2(3,4(CN)_25NH_2oz)]_2$	Light yellow	13.9 (14.2)	61.5 (62.0)	8.61 (9.1)	3.9 (4.1)	1527.1 (1527.6)

their complexes. The i.r. spectra of the compounds exhibit the complete absence of N-H stretching mode expected to appear at 2920cm^{-1} in the free ligand and 3440cm^{-1} upon coordination suggesting deprotonation at pyrrolic nitrogen N(1) leading to the formation of 4-cyano-5-aminopyrazolide ion, [4CN5NH$_2$pz]$^-$ or 3,4-dicyano-5-aminopyrozolide ion, [3,4(CN)$_2$5NH$_2$pz]$^-$. However, the other bands corresponding to the pyrazole ring vibrations (R_1, R_2, R_3 and R_4) and the substituent groups CN and NH$_2$ appear at their estimated positions as recorded for the ligand except a negative shift (10-20cm^{-1}) in C=N stretching vibration (Table 2). The absence of N-H stretching vibration and a slight negative shift in νC=N suggest the involvement of both the nitrogens, pyridyl, N(2) as well as pyrrolic, N(1) in bonding in basic reaction medium such that the pyrazolide ions act as bridge between the metal ions producing polymeric compounds, [M,4CN5NH$_2$pz] or [M3,4(CN)$_2$5NH$_2$pz] with metal (I) chlorides with their possible structure as depicted below:

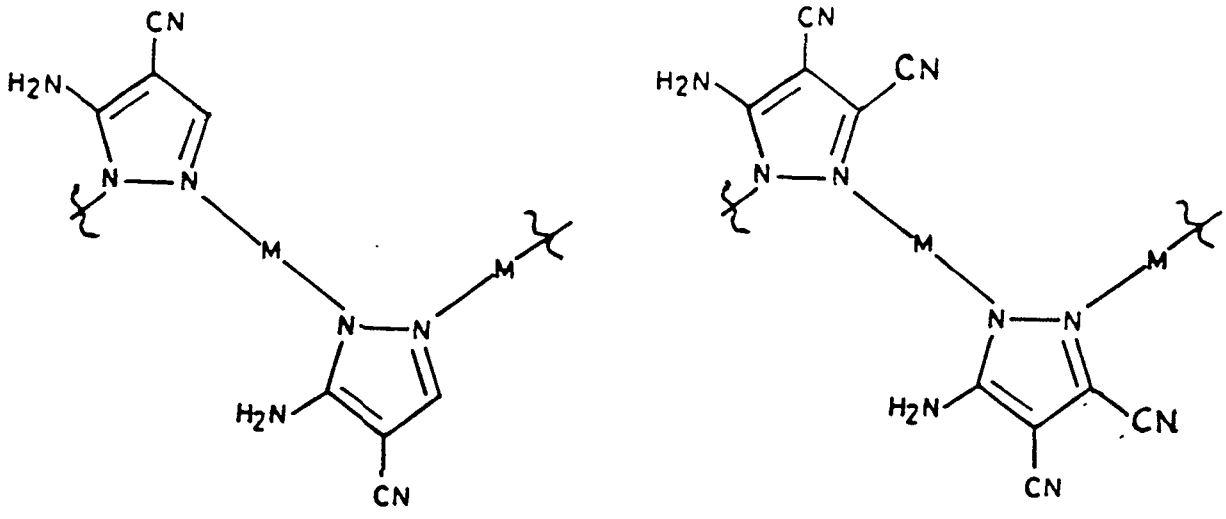
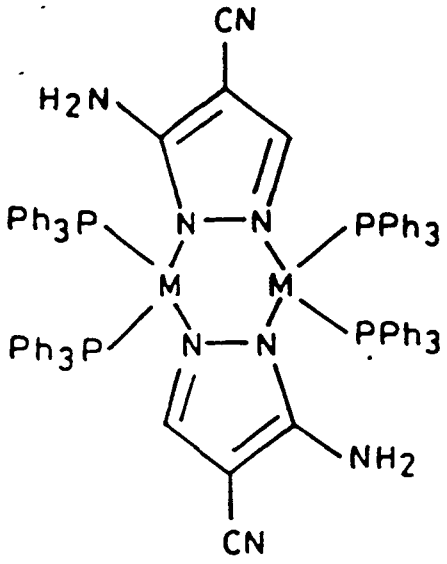


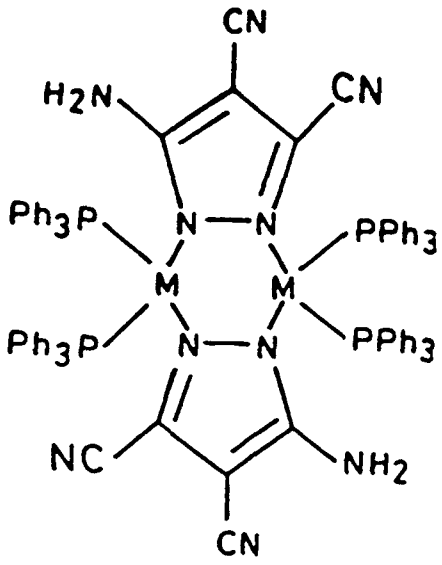
Table :2 Infra-red Vibrational Frequencies (cm-1) of the Compounds Derived from $[4CN5NH_2pz]^-$ or $[3,4(CN)_25NH_2pz]^-$.

Compounds	NH_2	Ring Vibrations	ν_{C-H}	$\nu_{C=N}$	$\nu_{C\equiv N}$	ν_{M-N}	PPh_3	ν_{M-P}
$[Cu(4CN5NH_2pz)]_n$	3410s 3355s 3315m 1610vs	1490s 1390m 1340s 940m	3150s 1065s 870m	1475m	2250vs	230s	-	-
$[Cu(3,4(CN)_25NH_2pz)]_n$	3410s 3355s 3310m 1610vs	1490s 1385m 1345s 940m	3150s 1060s 1045s 880m	1475m	2250vs	230s	-	-
$[Ag(4CN5NH_2pz)]_n$	3405s 3345s 3330s 1610vs	1480s 1380m 1325s 935w	3145s 1065s 1030s 880m	1480m	2250vs	235s	-	-
$[Ag(3,4(CN)_25NH_2pz)]_n$	3405s 3340s 3325s 1610vs	1475s 1375m 1330s 935w	3145s 1070s 1035s 885m	1485m	2250vs	235s	-	310m
$[Co(PPh_3)_2(4CN5NH_2pz)]_2$	3400s 3355m 3320s 1615vs	1480s 1390m 1340s 950w	3150s 1065s 1035s 890w	1470m	2250vs	230s	1320s 1075s 725s 505s	315m
$[Co(PPh_3)_2(3,4(CN)_25NH_2pz)]_2$	3405s 3350m 3325s 1610vs	1475s 1390m 1345s 940w	3155s 1070s 1040s 895w	1475m	2250vs	235s	1320s 1080s 730s 510s	310m
$[Cu(PPh_3)_2(4CN5NH_2pz)]_2$	3400s 3350s 3320s 1610vs	1475s 1385m 1340s 940s	3155s 1065s 1035s 890m	1470m	2250vs	230s	1320s 1075s 725s 505s	315m
$[Cu(PPh_3)_2(3,4(CN)_25NH_2pz)]_2$	3410s 3350m 3330s 1610vs	1470s 1380m 1345s 945w	3150s 1075s 1040s 890w	1475m	2245vs	220s	1430s 1090s 740s 500s	320m
$[Ag(PPh_3)_2(4CN5NH_2pz)]_2$	3401s 3345s 3310m 1610vs	1485s 1380m 1335s 940w	3150s 1065s 1030s 880m	1470m	2250vs	235s	1425s 1080s 740s 510s	310s
$[Ag(PPh_3)_2(3,4(CN)_25NH_2pz)]_2$	3400s 3350m 3310s 1610w	1480s 1375m 1335s 945w	3155s 1065s 1030s 880m	1480m	2250vs	235s	1420s 1080s 730s 500s	320s

s = strong, vs = very strong, m = medium, w = weak.

The Pyrazolide bridged dimeric species, $[M(PPh_3)_2(4CN5NH_2pz)]_2$ or $[M(PPh_3)_2\ 3,4\ (CN)_25NH_2pz]_2$ with $[M(PPh_3)_3X]$ where the polymerization is avoided due to the presence of encapping PPh_3 groups. The presence of PPh_3 as blocking groups has been confirmed by the characteristic bands corresponding to PPh_3 as well as a medium intensity band in 310-320 cm^{-1} region assignable to M-P stretching mode. A strong intensity band in 220-230 cm^{-1} region may, reasonably, be assigned to M-N stretching vibration. All the complexes are diamagnetic as expected. On the basis of present data the probable structure of these compounds may be visualized as below :





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CHAPTER - V

SYNTHESIS AND CHARACTERIZATION OF DIMERIC COMPLEXES OF 3-MERCAPTO-1, 2-PROPANEDIOL AND ITS 1-METHOXY AND 1-ETHOXY DERIVATIVES WITH TRIPHENYL PHOSPHINE DERIVATIVES OF COBALT (I), COBALT (II), COPPER (I), COPPER (II), AND SILVER (I).

INTRODUCTION

Considerable interest has been shown recently in the properties and reactions of metal complexes of ligand containing sulfur donors[1-4]. A number of metal compounds with either thiolato or phenolato ligands have been abundantly reported[5,6] for the simulation of either the active site structures of redox properties of metalloenzymes. Thiolates, as HS^- and S^{2-}, have been found to be versatile ligands, coordinating to one, two or three metals. The triple bridge coordinating mode is relatively rare and occur in cages and clusters, which are formed in a spontaneous and uncontrolled way[1,7]. Recently the synthesis and structure of diolefin trinuclear complexes of rhodium and iridium bridged thiolate ligands have been reported[4].

A study of sulfur containing metalloenzymes indicates the presence of M-S and/or M-O bonds essential to their biological activities. For example, the vanadium in O_2S_3 environment has been recently identified second nitrogenase[8-11]. The development of vanadium chemistry has been proved to be essential to understand its biological role in organism such as tunicates[12] which contain tunichrome[13] with vanadium (III) chelated to polypetide chains rich in hydroxyl groups. The four or five coordinate cobalt (II) thiolates have been considered as models for the catalytic site of the cobalt substituted alcohol dehydrogenase[14]. The vanadium (II), cobalt (III), chromium (III), manganese(II) and copper (II) complexes

of EHPG [ethylene bis(O-hydroxyphenyl) glycine] have been studied as models for metallotransferrins[15,16].

A mercaptide ion often retains its tendency to form S bridges even in the presence of other groups capable of coordination, but in these cases the extent of polymerization is often restricted to the formation of dimers[17,18]. One property of S bridges compound is that of low reactivity towards reagent such as p-toluidine and certain organic halides[19].

Recently a few dinuclear, trinuclear and dimeric complexes of 2-mercaptophenol have been reported[20-22]. The ligational behaviour of 3-mercapto-1, 2-propanediol (RSH) has been investigated[23] with copper (II), silver (I) and gold (III) ions producing polymeric species of the type $-[-MSR-M-SR-]_n$ where the copper (II) and gold(III) ions have been reduced to copper (I) and gold (I), respectively.

This chapter deals with the synthesis and physico-chemical studies on the complexes of 3-mercapto-1, 2-propanediol and its 1-methoxy and 1-ethoxy derivaties with triphenyl phosphine derivatives of cobalt (I), Cobalt (II), copper (I), Copper (II) and silver(I).

EXPERIMENTAL

Starting Materials

3-Mercapto-1, 2-propanediol (Aldrich), CH_3I and C_2H_5I (BDH) were commercially pure and used as such. The compounds $[M(PPh_3)_3X]$ [M=Co, Cu for X = Cl, and Ag for X = NO_3] and $[M(PPh_3)_2 Cl_2]$ [M=Co, Cu] were prepared by reported methods[24-26]. Tetrahydrofuran (THF) and Et_2O were purified and dried before their use. However, the 1-methoxy and 1-ethoxy deriatives of 3-mercapto-1, 2-propanediol were derived by method given below:

Preparation of 1-methoxy and 1-ethoxy derivatives of 3-mercapto-1, 2-propanediol, $[HSCH_2CH(OH)CH_2OR']$ [R' = CH_3, C_2H_5].

0.1 Mol of 3-mercapto-1, 2-propanediol was reacted with 0.12 mol sodium at room temperature and the reaction mixture was stirred for 3 hrs. The unreacted sodium was filtered through Schlenk filteration frit. The filterate was then reacted with 0.1 mol of methyliodide or ethyliodide. The precipitated NaI was again filtered and the resulting viscous ligands were identified as $[HSCH_2CH(OH)CH_2OCH_3]$ and $[HSCH_2CH(OH)CH_2OC_2H_5]$, respectively. On the basis of molecular weight determination and i.r. spectral studies such that only the primary alcoholic group reacted with sodium metal. Molecular weight found (calcd.) 122.16 (122.96) and 136.17 (136.10) for $HSCH_2CH(OH)CH_2OCH_3$ and $HSCH_2CH(OH)CH_2OC_2H_5$ respectively.

Preparation of the complexes of 3-mercapto-1, 2-propanediol with [$M(PPh_3)_3X$] [M = Co(I), Cu (I); X = Cl or Ag(I), X = NO_3] and [$M(PPh_3)_2Cl_2$] [M = Co(II), Cu(II)].

Bis (3-mercapto-1, 2-propanediol) bis (triphenylphosphine) Metal (I)

[$M(PPh_3)_2SCH_2CH(OH)CH_2OH$] ; [M = Co (1), Cu(2), Ag (3)].

To 0.020 mol of [$M(PPh_3)_3X$] [X = Cl for Co and Cu, X=NO_3 for Ag] dissolved in THF, 3-mercapto-1, 2-propanediol (0.025 mol) was slowly added under dry N_2 atmosphere at room temperature. The reaction mixture was magnetically stirred for 1 hr. resulting in the isolation of solid products which was filtered off, washed several times with THF followed by Et_2O and vacuum dried. The mother liquor obtained after filteration and washing was evaporated leaving behind a colourless, microcrystalline solid mass in each case identified as PPh_3 confirmed on the basis of microanalysis, m.p. and i.r. spectral studies.

Bis (3-mercapto-1, 2-propanediol) bis (triphenylphosphine) Metal (I)

[$M(PPh_3)_2\ SCH_2\ CH(OH)CH_2OH]_2$, [M = Co (1'), Cu(2')]

0.020 Mol of [$M(PPh_3)_2\ Cl_2$] solution in THF was slowly reacted with 0.025 mol of the ligand solution in THF under dry N_2 at room temperature. The reaction mixture was continuously stirred for 1 hr. resulting in the isolation of solid products

which was filtered, washed several times with THF followed Et_2O and dried in vacuuo.

Bis [3-mercapto-1-methoxypropane-2-ol] bis(triphenylphosphine) Metal (I)

$[M(PPh_3)_2SCH_2CH(OH)CH_2OCH_3]$, [M = Co (1a), Cu(2a), Ag(3a)]

0.01 Mol of precursor [$M(PPh_3)_3X$] taken in 50 cm^3 of THF was reacted with 0.012 mol of $[SHCH_2CH(OH)CH_2OCH_3]$ under dry N_2 atmosphere at room temperature. The reaction mixture was stirred for 2 hrs. to ensure completion of the reaction. The product thus formed was filtered off, washed several times with THF and finally with Et_2O. The mother liquor obtained after filteration and washings when evaporated resulted microcystalline solid identified as PPh_3 on the basis of microanalysis m.pt. and i.r. spectral studies.

Bis[(3-mercapto-1-methoxypropane-2-ol) bis(triphenylphosphine) Metal (I)

$[M(PPh_3)_2SCH_2CH(OH)CH_2OCH_3]$ [M = Co (1a'), Cu(2a')]

An excess of 3-mercapto-1-methoxypropane-2-ol (0.012 mol) in THF was slowly added to 0.01 mol of $[M(PPh_3)_2Cl_2]$ in THF under similar reaction conditions as described in the above methods, followed by magnetic stirring. This has resulted in the formation of solid products. The solids thus formed were filtered off using a Schlenk filteration assembly, washed several times with THF followed by Et_2O and vacuum dried.

Bis [3-mercapto-1-ethoxypropane-2-ol)bis(triphenylphosphine)] Metal (I)

$[M(PPh_3)_2SCH_2CH(OH)CH_2OC_2H_5]_2$ [M = Co (1b), Cu (2b), Ag(3b)]

A solution of the ligand (0.012 mol) was slowly added to a solution of precursors [M $(PPh_3)_3$ X] (0.01 mol) in THF under N_2 atomosphere at room temperature. The reaction mixture was stirred resulting in the formation of solid which was isolated in a manner described above. The mother liquor left colourless microcrystalline solid mass identified as PPh_3 on evaporation.

Bis[(3-mercapto-1-ethoxypropane-2-ol)bis(triphenylphosphine)] Metal (I)

$[M(PPh_3)_2SCH_2CH(OH)CH_2OC_2H_5]_2$ [M = Co(1b'), Cu(2b')]

A solution of $[M(PPh_3)_2Cl_2]$ (0.01 mol) in THF was slowly added with continuous stirring to a solution of the ligand (0.012 mol) under dry N_2 atmosphere at room temperature. This has resulted in the seperation of solid product which was isolated in a manner described earlier.

Analysis and Physical Measurements

Elemental analyses were carried out in the micro-analytical laboratory of CDRI Lucknow. The metals were estimated by EDTA titration[27] and gravimetric[28] methods. IR spectra (4000-200 cm^{-1}) were recorded as KBr discs on a Perkin Elmer 621 spectrophotometer. The reflectance spectra of

compounds using MgO as calibrant were recorded on Carl-Zeiss VSU-2P spectrophotometer at room temperature. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. Molecular weights of the compounds were determined using camphor as solvent by Rast's method[29].

RESULTS AND DISCUSSION

The results of elemental analyses (Table-1) of the complexes derived from the reaction of 3-mercapto-1, 2-propanediol and its 1-methoxy and 1-ethoxy derivatives, [$HSCH_2CH(OH)CH_2OR'$] [R' = H, CH_3, C_2H_5], RSH [R = CH_2 CH(OH). CH_2OR'] WITH [$M(PPh_3)_3$ X] [M = Co(I), Cu(I), X = Cl or Ag(I). X = NO_3] are formed in 1: 1 stoichiometry having the composition as [$M(PPh_3)_2RS]_2$ liberating one mole equivalent of free triphenylphosphine. However, the reaction of RSH with [$M(PPh_3)_2Cl_2$] [M = Co(II), Cu(II)] under similar reaction conditions produced the complexes with the stoichiometry as 1:1 and their composition as [M $(PPh_3)_2RS]_2$ where the metal ions have been reduced to their corresponding monovalent states. The polymerization in these cases has been avoided due to the presence of encapping PPh_3 groups similar to that reported[17,18] earlier.The experimental molecular weights (Table.1) confirm the dimeric nature whilst the low electrical conductivity values reveal their covalent nature.

The IR spectra of these compounds have been deduced by comparing the characteristic band positions obtained in the free ligands[23], RSH. The IR spectra of all the compounds show a complete absence of the S-H stretching vibration appearing as a strong band at ~2550 cm^{-1} in the spectrum of the free ligand. Two new medium intensity bands in the 340-390 cm^{-1} region may, reasonably, be assigned to νM-S. The confirmation regarding the involvement of the primary alcoholic oxygen of

Table-1 : Elemental Analysis, Molecular Weights and Molar Conductivities of the Compounds

Compounds		Yield (%)	Colour	Found (Calcd) (%) M	S	C	H	Molecular weight Found[a] (Calc.)	Molar conductivity[b] ($Cm^2 Ohm^{-1} mole^{-1}$)
$[Co(PPh_3)_2RS]_2$	(1)	75	Greenish-yellow	8.1 (8.5)	4.2 (4.6)	67.2 (67.2)	4.8 (5.2)	1375 (1380)	27
$[Co(PPh_3)_2RS]_2$	(1a)	65	Light-green	7.8 (8.3)	4.1 (4.5)	65.9 (66.4)	4.9 (5.2)	1403 (1408)	29
$[Co(PPh_3)_2RS]_2$	(1b)	69	Light-green	7.6 (8.2)	3.9 (4.4)	68.0 (68.4)	5.1 (5.6)	1431 (1436)	30
$[Co(PPh_3)_2RS]_2$	(1′)	68	Greenish-yellow	8.0 (8.4)	4.7 (4.6)	67.2 (67.6)	5.0 (5.2)	1377 (1382)	28
$[Co(PPh_3)_2RS]_2$	(1a′)	70	Light-green	7.9 (8.3)	4.3 (4.5)	66.0 (66.4)	4.8 (5.2)	1404 (1410)	31
$[Co(PPh_3)_2RS]_2$	(1b′)	72	Light-green	7.8 (8.1)	4.0 (4.4)	67.9 (68.4)	5.3 (5.6)	1434 (1438)	27
$[Cu(PPh_3)_2RS]_2$	(2)	65	Colour-less	9.8 (9.1)	4.3 (4.6)	67.0 (67.4)	5.0 (5.2)	1384 (1389)	32
$[Cu(PPh_3)_2RS]_2$	(2a)	69	Colour-less	9.3 (8.9)	4.1 (4.5)	67.3 (67.6)	5.1 (5.4)	1412 (1417)	30
$[Cu(PPh_3)_2RS]_2$	(2b)	70	Colour-less	8.1 (8.7)	4.0 (4.4)	67.6 (68.0)	5.3 (5.6)	1440 (1445)	35
$[Cu(PPh_3)_2RS]_2$	(2′)	59	Colour-less	8.8 (9.1)	4.3 (4.5)	66.9 (67.2)	4.8 (5.2)	1384 (1391)	30
$[Cu(PPh_3)_2RS]_2$	(2a′)	67	Colour-less	8.6 (8.9)	4.0 (4.5)	61.2 (67.6)	5.2 (5.4)	1415 (1419)	32
$[Cu(PPh_3)_2RS]_2$	(2b′)	70	Colour-less	8.3 (8.7)	4.3 (4.4)	67.8 (68.0)	5.4 (5.6)	1442 (1447)	36
$[Ag(PPh_3)_2RS]_2$	(3)	75	Gray	14.1 (14.5)	3.9 (4.3)	62.9 (63.2)	4.7 (5.0)	1472 (1475)	29
$[Ag(PPh_3)_2RS]_2$	(3a)	70	Grayish-white	13.9 (14.3)	4.0 (4.2)	63.2 (63.6)	4.8 (5.0)	1501 (1506)	29
$[Ag(PPh_3)_2RS]_2$	(3b)	72	Grayish-white	13.8 (14.0)	3.7 (4.1)	63.7 (64.0)	4.9 (5.2)	1530 (1534)	30

[a] In camonor; [b] In Dimethyl sulonoxide for the 1mM solution.

R = $CH_2CH(OH)CH_2OR'$ R′ = H for (1), (1′), (2), (2′), (3); CH_3 for (1a), (2a), (1a′), (2a′), (3a);

C_2H_5 for (1b), (2b), (1b′), (2b′), (3).

the ligands in coordination may be inferred by comparing the position of νC-O with the complexes derived from the bridged alkoxides[30] . The IR spectra of the compounds obtained from 1-methoxy and 1-ethoxy derivatives of 3-mercapto-1, 2-propanediol do not exhibit band in the frequency 1030-1050cm^{-1} range reported for bridged OCH_3 or OC_2H_5 groups in the metal alkoxides suggesting the non-involvement of the primary oxygen in coordination contrary to that reported[23] in polymeric complexes of 3-mercapto-1,2-propanediol with Cu(I), Ag(I) and Au(I). However, the appearance of a strong band in the 1060-1070 cm^{-1} region corroborates the existence of free OCH_3 or OC_2H_5 groups in the complexes. The bands observed in the 1020-1030 cm^{-1} region in 3-mercapto-1, 2-propanediol and its complexes (1), (1'), (2), (2'), and (3) may then be unambiguously assigned for the C-O str. of the primary alcoholic groups. The bands characteristic of Ph_3P and νM-P appear in their expected positions. The following possible structure may be proposed based on IR spectral findings.

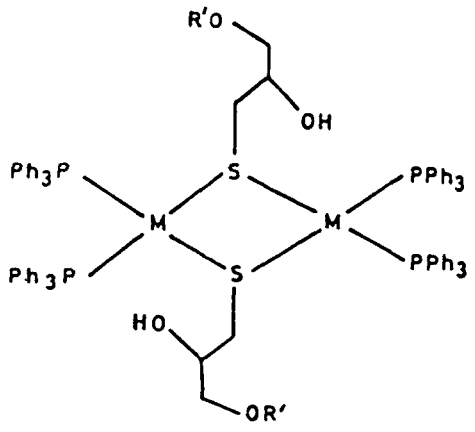

Table-2 : I.R. Vibrational Frequencies (cm-1) of the Free Ligand and its Complexes.

Compound	ν S-H	ν C-O (Secondary)	ν C-O (Primary)	ν O-CH_3 ν O-C_2H_5	ν C-S str.	ν M-S str.	ν M-P str.	PPh_3
$SHCH_2(OH)CHCH_2OH$	2250s	1085s	1030sb	-	635m	-	-	-
$SHCH_2(OH)CHCH_2OCH_3$	2240s	1060s	-	1065s	625m	-	-	-
$SHCH_2(OH)CHCH_2OC_2H_5$	2245s	1055s	-	1070s	630m	-	-	-
(1)	-	1080s	1020sb	-	625m	340m 360m	320m	1420s 1090s 730s
(1a)	-	1055s	-	1060s	630m	350m 375m	310m	1430s 1080s 730s
(1b)	-	1050s	-	1070s	625m	345m 380m	315m	1425s 1085s 730s
(1')	-	1080s	1025sb	-	635m	340m 370m	320m	1430s 1090s 730s
(1a')	-	1060s	-	1065s	630m	355m 380m	310m	1430m 1090s 720s
(1b')	-	1055s	-	1065s	625m	350m 375m	315m	1420s 1070s 725s
(2)	-	1080s	1020sb	-	630m	345m 385m	320m	1430s 1080s 730s
(2a)	-	1055s	-	1065s	635m	350m 390m	315m	1420s 1090s 720s
(2b)	-	1050s	-	1060s	625m	345m 390m	310m	1430s 1085s 730s
(2')	-	1080s	1025sb	-	630m	340m 380m	310m	1425s 1080s

Contd...

Compound	ν S-H	ν C-O (Secondary)	ν C-O (Primary)	ν O-CH_3 ν O-C_2H_5	ν C-S str.	ν M-S str.	ν M-P str.	PPh_3
								720s
(2a')	-	1065s	-	1060s	625m	330m 380m	315m	1430s 1085s 720s
(2b)	-	1055s	-	1070s	630m	335m 370m	320m	1420s 1090s 730s
(3)	-	1080s	1020sb	-	625m	350m 390m	315m	1425s 1090s 730s
(3a)	-	1060s	-	1070s	630m	325m 375m	320m	1430s 1090s 730s
(3b)	-	1055s	-	1065	620m	330m 380m	315m	1425s 1080s 720s

Measurements on the magnetic properties of compounds(2), (3), (2a), (3a), (2b), (3b), (2'), (2a') and (2b') indicated that they are diagmagnetic. However, magnetic moment values (Table 3) obtained for compounds (1), (1a), (1b), (1'), (1a') and (1b') lie in the range comparable to that reported for Co(I) complexes having tetrahedral geometry. This has been further confirmed by the band positions in the reflectance spectra of these compounds (Table 3). The reflectance spectra exhibit an intense band in 14,690-14,800 cm^{-1} region which may, reasonably, be assigned for $^{3}T_{1g}(F) \longrightarrow {}^{3}T_{1g}(P)$ transition.

Table-3: μeff (B.M.) and Ligand Field Bands observed in the Reflectance in cm^{-1} and their Assignment.

Compound	μ eff	Band Position (cm^{-1})	Assignments
(1)	3.0	14,690	$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$
(1a)	3.2	14,740	$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$
(1b)	3.4	14,800	$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$
(1')	3.1	14,700	$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$
(1a')	3.2	14,750	$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$
(1b')	3.4	14,800	$^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$

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CHAPTER - VI

SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON FIRST ROW TRANSITION METAL COMPLEXES OF SCHIFF BASE MACROCYCLE CONTAINING THE FURANYL MOIETY.

INTRODUCTION

Macrocyclic chemistry is developing at a fast rate because of its variety of applications[1-5], particularly as the model for naturally occuring metalloproteins. The obsevation that many of the natuaral and monocarboxylic acid antibiotics capable of complexing with main group metal cations and effecting their transfer across natural or synthetic membranes contain the 2,5-dimethyl tetrahydro furanylgroup has stimulated interest in the synthesis of macrocyclic ligands containing furanyl group[6]. Tetraimine Schiff base macrocycles have generally been synthesized, and thier metal complexes, through the (2+2) condensation of heterocyclic dicarbonyls and 1,n-diaminoalkanes in presence of alkaline earth or main group metals as template[7]. This technique is particularly applicable when pyridine or furan dicarbonyls are employed as the 'head' units for macrocycle.

The synthesis of metal complexes of (2+2) tetraimine Schiff base macrocycles derived from heterocyclic dicarbaldehydes such as pyridine-2, 6-furan-2,5- and thiophen-2,5-dicarbaldehydes has claimed much recent attention[8-10]. The use of pyrrolyl moiety as a head unit has been reported to give mono-and homobinuclear copper (II) complexes of pyrrole-containing macrocycles derived from pyrrole-2, 5-dicarbaldehydes and 1,3-diamino propane and of pyrrole-2, 5-dicarbaldehydes itself.

The advent and exploitation of tetraimine Schiff base

macrocycles as binucleating ligands gave the oppurtunity to incorporate into these macrocycles aliphatic alcohols as lateral units and hence make provision for the possibility of hydrogen bridges[11-13].

Tetrahydroborate reduction of a range of Schiff base di-imine macrocycles, prepared by template cyclization reaction on mangnese (II) or lead (II) has afforded a series of structurally related metal free macrocycles incorporating both oxygen and nitrogen donor atoms giving all ten new rings are reported[14]. Physical measurements indicate that many of these rings forms 1:1 complexes with Co(II), Ni(II) and/or Cu (II). The stabilities of selected complexes have been determined using the potentiometric and (pH) titration technique. In all cases much greater stability for the complexes of Cu(II) relative to those Co(II) or Ni(II) was observed, the structural origin of this selectivity has been investigated by X-ray diffraction studies. These indicate that the comlexes of Ni(II) and Cu(II) have markedly different structures for one of the O_2N_3 type ligands. In the Ni(II) species the geometry is distorted octahedral with the macrocycles occupying four co-ordination positions with one ether oxygen not co-ordinated. The remaining (cis) co-ordination position are filled by nitrate ion. In the Cu(II) complexes the macrocycles folds such that an unsymmetrical but apparently favourable cavity is formed and all five donor atoms co-ordinated to the metal. A six co-ordination position is filled by a nitrate ion.

Use of thiophene 2,5-dicarboxaldehydes led to the synthesis of metal-free tetraimine Schiff base macrocycles and it was found that the use of a metal template was unnecessary[15]. This chapter deals with the sysnthesis and characterization of first row transition metal complexes of the type, (MLX_2) (M=Co (II), Ni(II), or Cu(II); X=Cl or SCN) with macrocyclic ligand, L containing furanyl unit.

EXPERIMENTAL

Starting Materials

2,5-diformylfuran was prepared as described in the litrature[16] while 1,3-diaminopropane was commercially available (E.Merck) used without further purification. $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.4H_2O$, $Co(SCN)_2$, $Ni(SCN)_2$ and $Cu(SCN)_2$ all reagents were reagent grade and solvents were dried according to the standard procedure just before their use.

Synthesis of Dichloro (23,24-dioxa-3,7,14,18-tetra-azacycloeicosa 1,2,7,9,11,13,18,20-Octaene) Metal (II), $MLCl_2$ [M = Co (II), Ni(II) and Cu (II)].

The complexes were prepared by mixing dry MeOH solution ($50cm^3$) of 2,5-diformylfuran (0.05 mol), 1,3-diaminopropane (0.05 mol) and the metal chlorides (0.025 mol) were taken individualy into three stoppered seperating funnels of 100 cm^3 size attached through each neck of the four necked flask with

joints. The fourth neck is used for the insertion of condenser for reflux purpose. The three solution were simultaneously added dropwise (~1h) through each neck of a four necked round bottom flask containing refluxing MeOH (50 cm^3). When the addition was complete the contents were refluxed for a further 76 h and the suspension so formed was collected by evaporation of the solvents. The products were purified by silica gel column chromatography using a mixture of EtOAc-MeOH (6:4V/V) as eluant. The purity of final product was checked by t.l.c. of solution of the complexes in DMF using EtOAc - MeOH (6:4V/V) as eluant, only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure.

Synthesis of Diisothiocyanato (23,24-dioxa-3,7,14,18-tetra-azacycloei cosa 1,2,7,9,11,13,18,20-octaene) Metal (II), $ML(NCS)_2$ [M = Co (II), Ni(II) and Cu (II)].

These complexes were prepared by mixing 0.050 mol of 2,5-diformylfuran, solution in MeOH (50cm^3) 1,3-diaminopropane (0.05 mol) and of 0.025 mol of the metal thiocynates taken seperately in three seperating funnels join to a four necked round bottom flask. . The three solution were slowly added dropwise through each neck of a four necked reaction flask which contain refluxing MeOH (50 cm^3). When the addition was completed the contents were refluxed for a long time and the suspension thus formed collected by evaporation of the solvent. The product was purified by silica gel column

chromatography using a mixture of EtOAc-MeOH (6:4V/V) as eluant. The purity of the final product was checked by t.l.c of solution of the complexes as described earlier.

RESULTS AND DISCUSSION

Reaction of 2,5-diformylfuran with 1,3-diaminopropane in methanol using 2:2 ratio led to gums, which appeared to be polymeric. However, if the reaction is carried out in the presence of a metal salts (chloride or thiocynate) of the metal ions cobalt (II), nickel (II) or copper (II), crystalline complexes of the macrocycle L are obtained. The reaction requires boiling under reflux for long periods (76 hr) which represents a dramatic demonstration of the template action of the metal ions.

The microanalytical results (Table 1) are consistent with the formulation of the comlexes as $[MLX_2]$ [M = Co(II), Ni(II), Cu(II), X = Cl, SCN]. The i.r. spectra of the complexes (Table 2) exhibit a single sharp absorption in the 1605-1635 cm^{-1} region is attributed to the imine band ν(C=N)[17]. No bands characteristic of free carbonyl group 1650-1700 cm^{-1} region or free amine generaly reported to occur in 3300-3500 cm^{-1} region were observed. A weak band in 405-425 cm^{-1} region in the i.r. spectra of the complexes may possibly be assigned for M-O stretching vibration suggesting the coordination

Table 1: Yeilds, Analytical and Mass Spectral Data for the Complexes.

Complex	Yeild	Found (Calcd.) (%)					M^+ (m/z)
		M	Cl	C	H	N	Found (Calcd.)
$[CoL(NCS)_2]$	35	11.2 (11.8)	-	42.4 (43.2)	4.1 (4.0)	11.1 (11.2)	498 (499)
$[NiL(NCS)_2]$	25	11.5 (11.8)	-	42.7 (43.3)	3.9 (4.0)	11.1 (11.2)	497 (499)
$[CuL(NCS)_2]$	30	12.1 (12.5)	-	43.1 (42.9)	4.1 (3.9)	11.0 (11.1)	501 (503)
$[Co\ L\ Cl_2]$	25	13.2 (13.0)	15.7 (15.5)	46.8 (47.6)	4.3 (4.4)	12.5 (12.3)	452 (453)
$[Ni\ L\ Cl_2]$	20	13.1 (13.0)	15.4 (15.4)	47.1 (47.5)	4.3 (4.1)	12.0 (12.3)	452 (453)
$[Cu\ L\ Cl_2]$	20	13.5 (13.7)	15.5 (15.3)	47.6 (47.2)	4.2 (4.3)	12.4 (12.3)	455 (457)

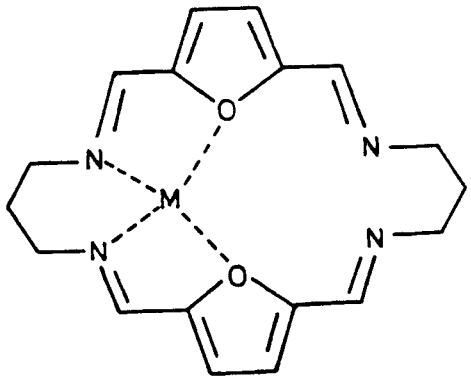

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Table 2: Characteristic i.r. bands (cm-1) for the complexes (KBr Pellets)

Complex	ν(C=N)	ν(C-H)	δ(C-H)	ν(C-O)	ν(C-N)	ν(M-N)	ν(M-O)	ν(M-Cl)	ν(M-NCS)
[CoL$(NCS)_2$]	1620	2940	1430	1125	1155	350	405	-	265
[NiL$(NCS)_2$]	1610	2930	1405	1110	1150	360	420	-	280
[CuL$(NCS)_2$]	1610	2940	1410	1000	1155	345	415	-	260
[Co L Cl_2]	1605	2925	1425	1125	1160	350	410	300	-
[Ni L Cl_2]	1635	2950	1445	1105	1175	345	425	285	-
[Cu L Cl_2]	1615	2945	1450	1050	1200	350	410	265	-

through furanyl oxygen. However, a medium intensity band in 345-360 cm^{-1} region may, reasonably, be assigned to M-N stretching vibration. The isothiocyanato complexes show bands at ca 2115cm^{-1} and 810cm^{-1} assignable to ν(CN) and ν(CS) respectively, whilst a new band at ca 260-280 cm^{-1} is assignable to ν(M-NCS) [18]. The chloro-complexes display bands assigned to ν(M-Cl) [19] (Table 2).

The ^{1}Hn.m.r. spectra of the soluble tetraimine macrocyclic complexes (Table 3) all show a singlet at ca 8.1-8.5 ppm corresponding to the four equivalent carboximine protons (4H, CH=N) plus a multiplet at 3.1-3.65 ppm due to the methylene protons [10] (12H, CH_2) of propane chain. A singlet at 7.1-7.6 corresponds to the furanyl ring protons[20] (4H, CH-furan). No signal assignable to aldehydic protons was detected. This information together with the i.r. data, demonstrates that the formation of the macrocyclic ligand has occured.

The observed magnetic moment values of cobalt complexes are consist with an octahedral geometry of their complexes. The reflectance spectra of the cobalt complexes exhibit two principal bands in 8100-8890 cm^{-1} region and in 17930-18500 cm^{-1} region which may reasonably be assigned to transition $^{4}T_{1g}(F) \longrightarrow {}^{4}T_{2g}(F)$ and $^{4}T_{1g}(F) \longrightarrow {}^{4}T_{1g}(P)$, respectively (Table 3) correponding to an octahedral geometry around the cobalt ion. However, a weak band appearing in

Table 3: 1H n.m.r. reflectance and magnetic dataa for the complexes in DMSO.

Complexes	HC=N	Ring protons	CH_2-C=N	μeff	Band position	Assignments
[CoL(NCS)$_2$]	8.5(s)	7.3(s)	3.5(m)	4.2	8890 16100 17930	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
[NiL(NCS)$_2$]	8.24(s)	7.2(s)	3.1(m)	3.2	10400 11500 18100 8530	$^3B_{1g} \rightarrow {}^3B_{2g}(F)$ $^3B_{1g} \rightarrow {}^3A_{2g}(F)$ $^3B_{1g} \rightarrow {}^3A_{1g}(P)$ $^3B_{1g} \rightarrow {}^1E_g(F)$
[CuL(NCS)$_2$]	8.35(s)	7.1(s)	3.25(m)	1.75	15400 17990	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$
[Co L Cl$_2$]	8.1(s)	7.3(s)	3.55(m)	4.9	8100 14850 18510	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
[Ni L Cl$_2$]	8.3(s)	7.35(s)	3.33(m)	3.0	10500 11650 18200 8150	$^3B_{1g} \rightarrow {}^3B_{2g}(F)$ $^3B_{1g} \rightarrow {}^3A_{2g}(F)$ $^3B_{1g} \rightarrow {}^3A_{1g}(P)$ $^3B_{1g} \rightarrow {}^1E_g(F)$
[Cu L Cl$_2$]	8.45(s)	7.6(s)	3.65(m)	1.8	17000 18750	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2E_g$

[a]Chemical shifts (δ/ppm) with multiplicities in parentheses.

14,850 - 16,100cm^{-1} region is formally a two electron transition and therefore logically assigned to $^4T_{1g}$ (F) $\longrightarrow$ $^4A_{2g}$(F) transition which is a characteristic feature of octahedral Co(II) complexes.

The observed magnetic moment for the complexes derived from Ni(II) ion is comparable to that the reported for a variety of six coordinate Ni(II) complexes. The electronic spectra, however, exhibit bands (Table 3) expected fora tetragonally distorted octahedral complex. The observed bands are assignable to $^3B_{1g} \longrightarrow {}^3B_{2g}$(F), $^3B_{1g} \longrightarrow {}^3A_{2g}$(F), $^3B_{1g} \longrightarrow {}^3A_{1g}$(P) and $^3B_{1g} \longrightarrow {}^3E_{1g}$ (F) transitions.

However, the magnetic moment of Cu(II) comlexes corresponds to a high spin distorted octahedral geometry[21]. This has been further substentained by appearance of two bands in the electronic spectra centered in 15400-1700cm^{-1} region and 17890-18750cm^{-1} region which may reasonably be assigned[22] to $^2B_{1g} \longrightarrow {}^2B_{2g}$ and $^2B_{1g} \longrightarrow {}^2E_g$ transitions.

PHYSICAL MEASUREMENTS :

I.r. spectra were recorded in the 4000-200 cm^{-1} range as KBr discs or nujol mulls using a Perkin-Elemer 577 spectrometer. ^{1}H n.m.r. spectra were determined in DMSO using

a Bruker WM 250 Fourier-transofrm instrument with Me_4Si as internal standard. Mass spectra were recorded using an AE1 MS902 spectrometer. Reflectance spectra were taken on a carl-Zein VSU-2P spectrophotometer using MgO as the reflectance standard.

C, H and N analysis were obtained from the microanalytical laboratories of CDRI , Lucknow (India). Chloride and metal analyses were done according to established methods[22, 23]. The magnetic susceptibility measurements were carried out with a vibrating sample magnetometer model 155 (EG and G Princeton) at 23°C.

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